



Fermi National Accelerator Laboratory

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**Final Results from the SDC Dopant Search for New
Green Wavelength Shifting (WLS) Fibers
VOLUME I**

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Final Results from the SDC Dopant
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Introduction

A scintillating tile/fiber design had been selected for the SDC calorimeter. It consisted of scintillator plates embedded with a wavelength shifting (WLS) fiber which was spliced to a clear fiber. Based on the results from previous radiation damage studies on different scintillating materials, SCSN38 had been chosen for the scintillating tile and BCF91 or Y7 for the WLS fiber. SCSN38 is a blue-emitting scintillator and both WLS fibers use K-27, a green-emitting compound, as dopant.

K-27 has a decay time of approximately 12 ns which is long in comparison to that of most blue-emitting materials. Of all the factors that affect the speed of the scintillator tile/fiber calorimeter, the lifetime of the green-emitting dopant is the dominant component. To increase the speed of the calorimeter, it would be desirable that the green WLS fibers utilized had lifetimes between 3 and 5 ns. However, currently available green WLS fibers exhibit decay times between 7 and 12 ns. Development of new green-emitting WLS fibers with short decay times must be investigated.

The goal of this project was to search for commercially available fluorescent compounds with $\lambda_{abs}=400\text{--}450$ nm, $\lambda_{em}=450\text{--}550$ nm, $\tau=3\text{--}7$ ns, and quantum efficiency of minimum 0.7 (current K-27 baseline). Large Stokes shift and low self-absorption were not important requirements since the optical pathlength for the shifted light was small. Characterization of the spectroscopic properties of these compounds after styrene polymerization is important since this is an essential part of the manufacturing of WLS fibers.

Organic compounds fluorescing in the region of interest were purchased from Aldrich, Exciton, Lambda Physics, and Eastman Kodak. Polystyrene samples doped with these compounds were prepared in the chemistry laboratory of the Particle Detector Group. The samples had a dopant concentration of 0.02% by weight, with the exception of some dopants which presented solubility problems. In such cases, 0.01% (by weight) solutions were prepared. When the dopants were insoluble even at low concentrations, a crown-ether (C-E) was used as a solubilizing agent. Bulk polymerization of doped styrene solutions was carried out in Pyrex test tubes immersed in a silicone oil bath. After polymerization, the plastic rods were cut into 1-cm thick disks and polished. These disks were then used in all the measurements performed. Transmittance and fluorescence measurements were recorded by the Particle

Detector Group. Light yield and lifetime determinations were performed by SDC members using their setup at Laboratory 5.

Transmittance and fluorescence spectra were recorded with a Hewlett-Packard model 8451A diode array spectrophotometer. All transmittance measurements used undoped polystyrene as the reference. The fluorescence spectra were measured using an external Hg lamp whose light was brought into the spectrophotometer by means of a quartz fiber. Different excitation wavelengths were selected with the use of bandpass filters. Both back-surface (BS) and front-surface (FS) excitation measurements were performed. In the former, light from the quartz fiber excited the sample surface that faced away from the spectrophotometer collection optics. The sample fluorescence was thus viewed through the sample. In the front-surface (FS) excitation measurements, the quartz fiber was positioned so that the UV light excited the sample surface facing the spectrophotometer optics. In this case, the fluorescence was viewed directly and not through the sample. In both geometries, a 45° angle of incidence with respect to the surface plane was used.

For general characterization of the dopants, fluorescence data were recorded using a 313-nm excitation wavelength which is a region where most organic materials absorb and is commonly used in plastic scintillator studies. Nonetheless, the most representative fluorescence measurement is that using an excitation wavelength approximately at 430 nm since it is the wavelength closest to the actual emission of the blue tiles. Some samples would not absorb at such long wavelengths and 360 nm was selected. Other excitation wavelengths used were 400 and 450 nm.

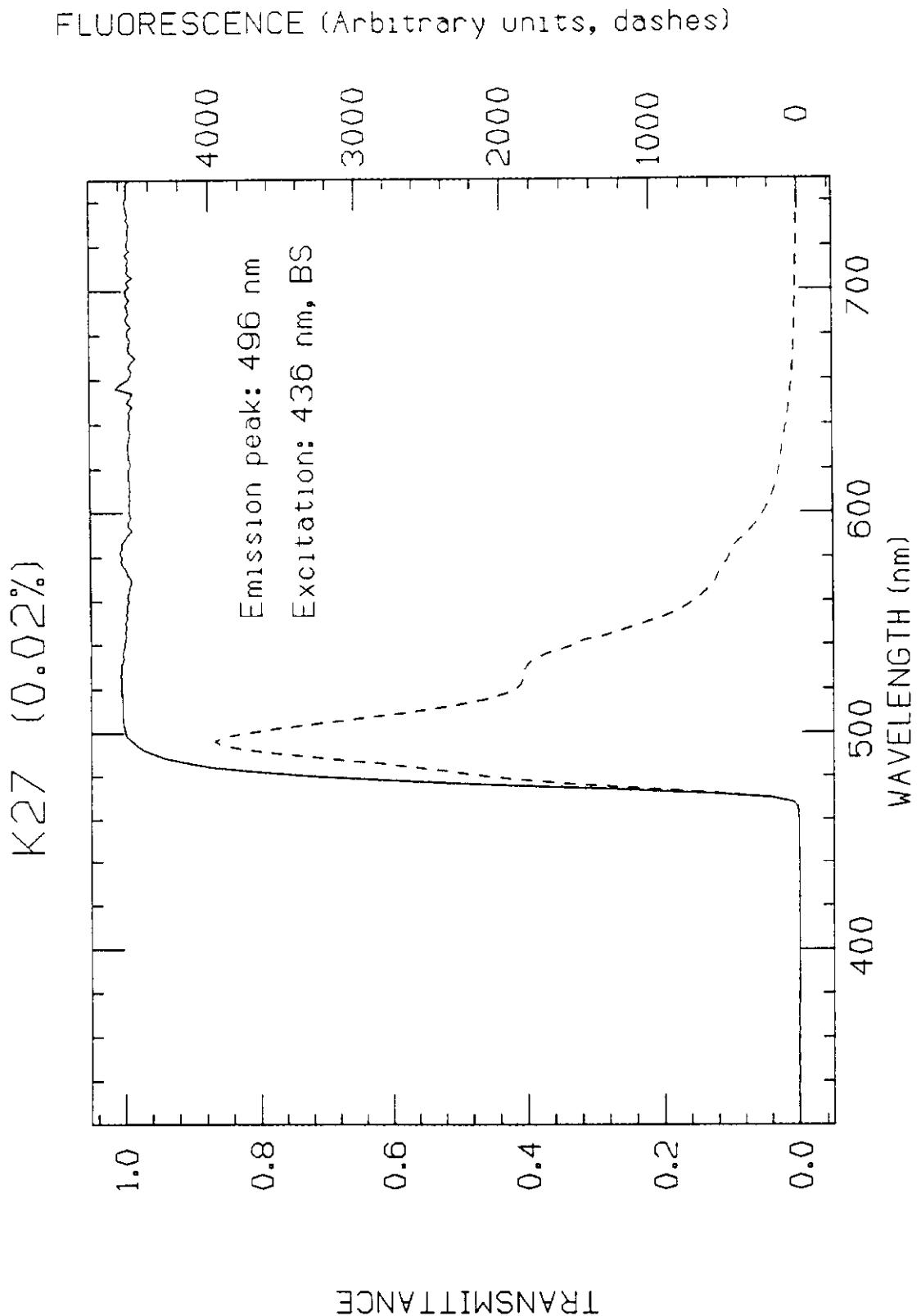
Radiation damage studies were also performed on these samples after the characterization studies were finished. For our convenience, the samples were irradiated in two sets; radiation damage set numbers 20 and 22. Changes in transmittance and light yield were recorded at different stages of the study.

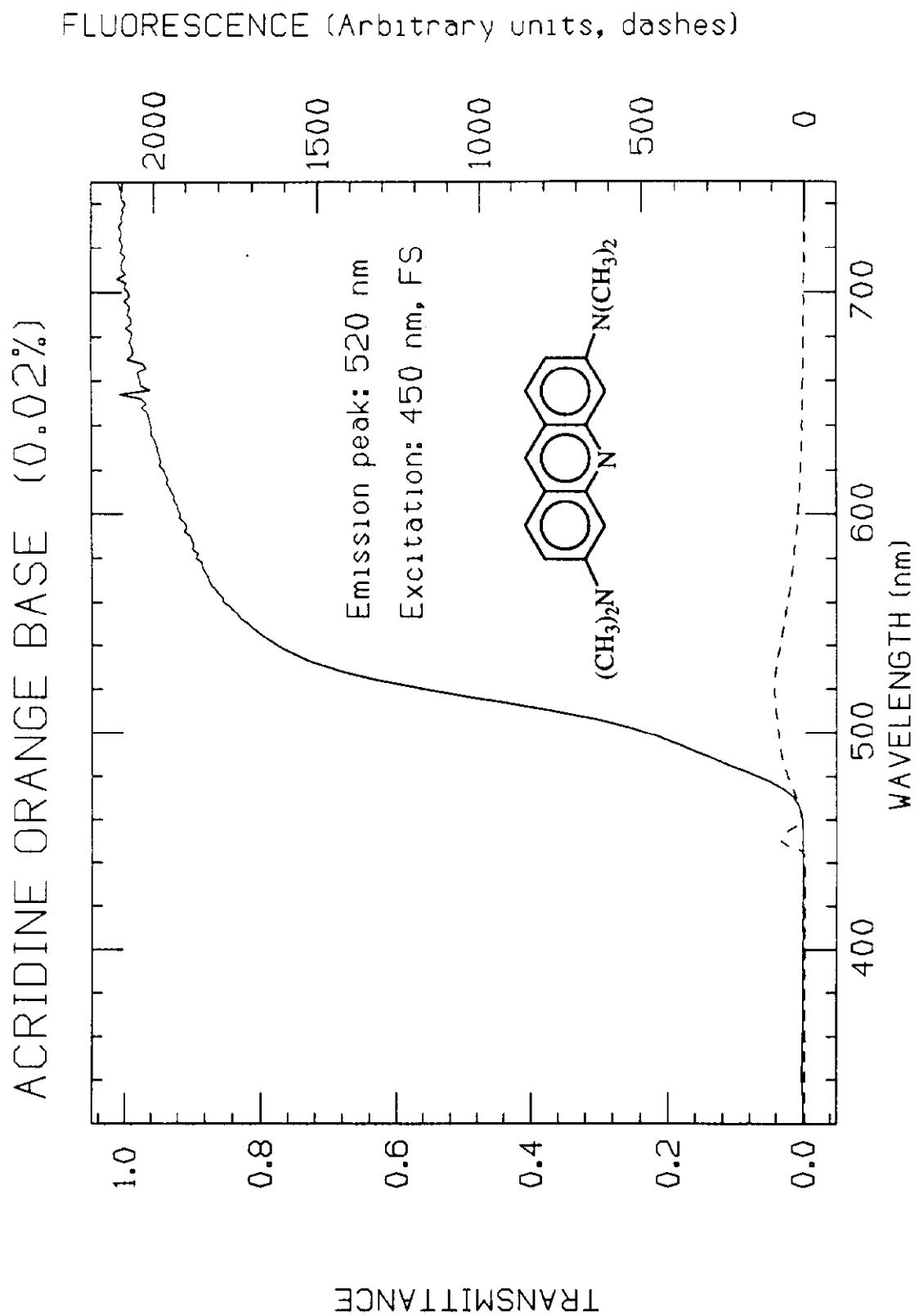
This summary presents the transmittance and fluorescence data for each dopant tested. However, many fluorescence measurements using different excitation wavelengths and orientations were recorded. These data have been compiled in the current two volumes. Volume I presents a plot for each dopant combining transmittance and the most representative fluorescence measurement. Volume II contains the remaining fluorescence plots which can be used as support data.

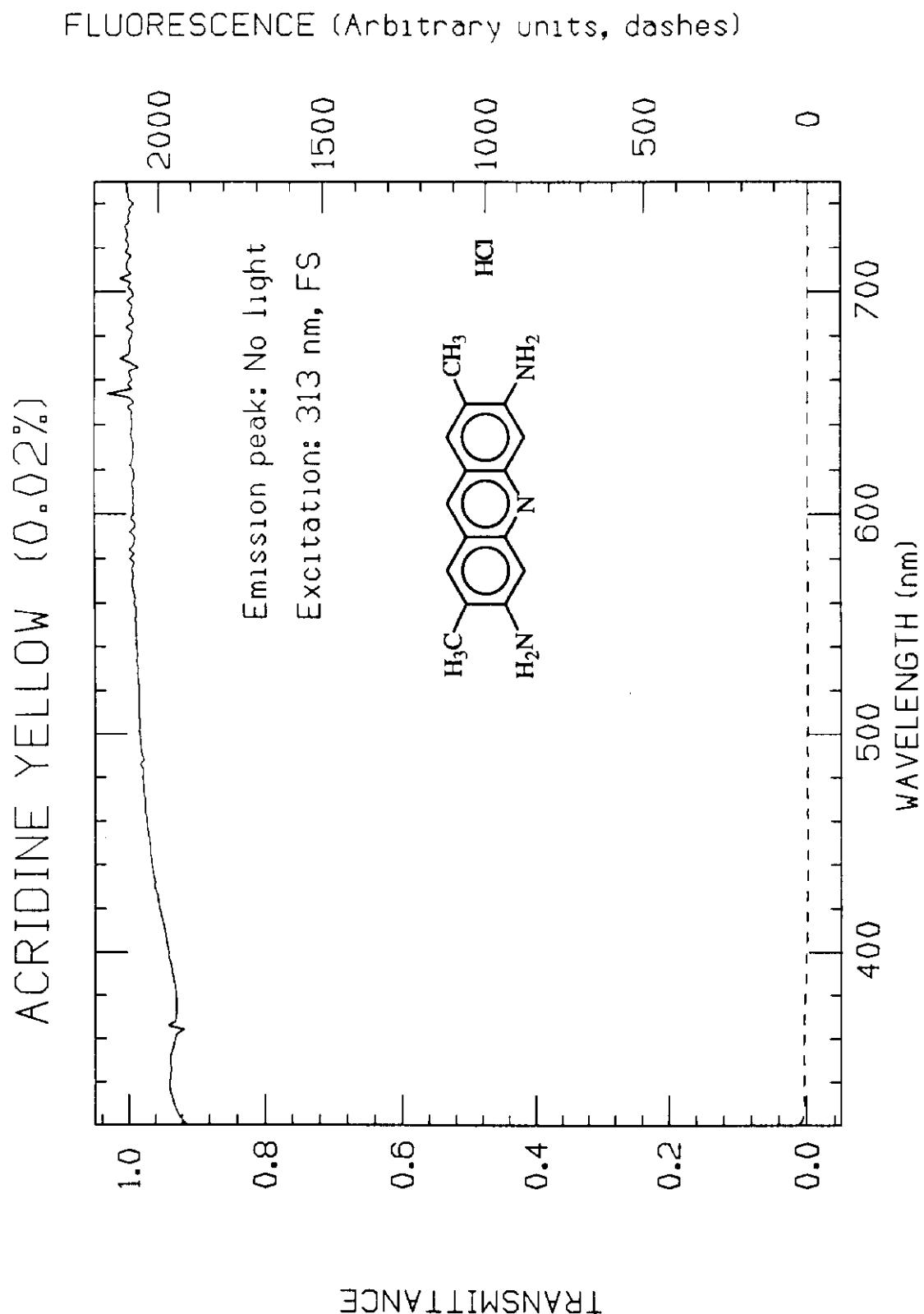
There are three appendices at the end of Volume I. Appendix A lists the

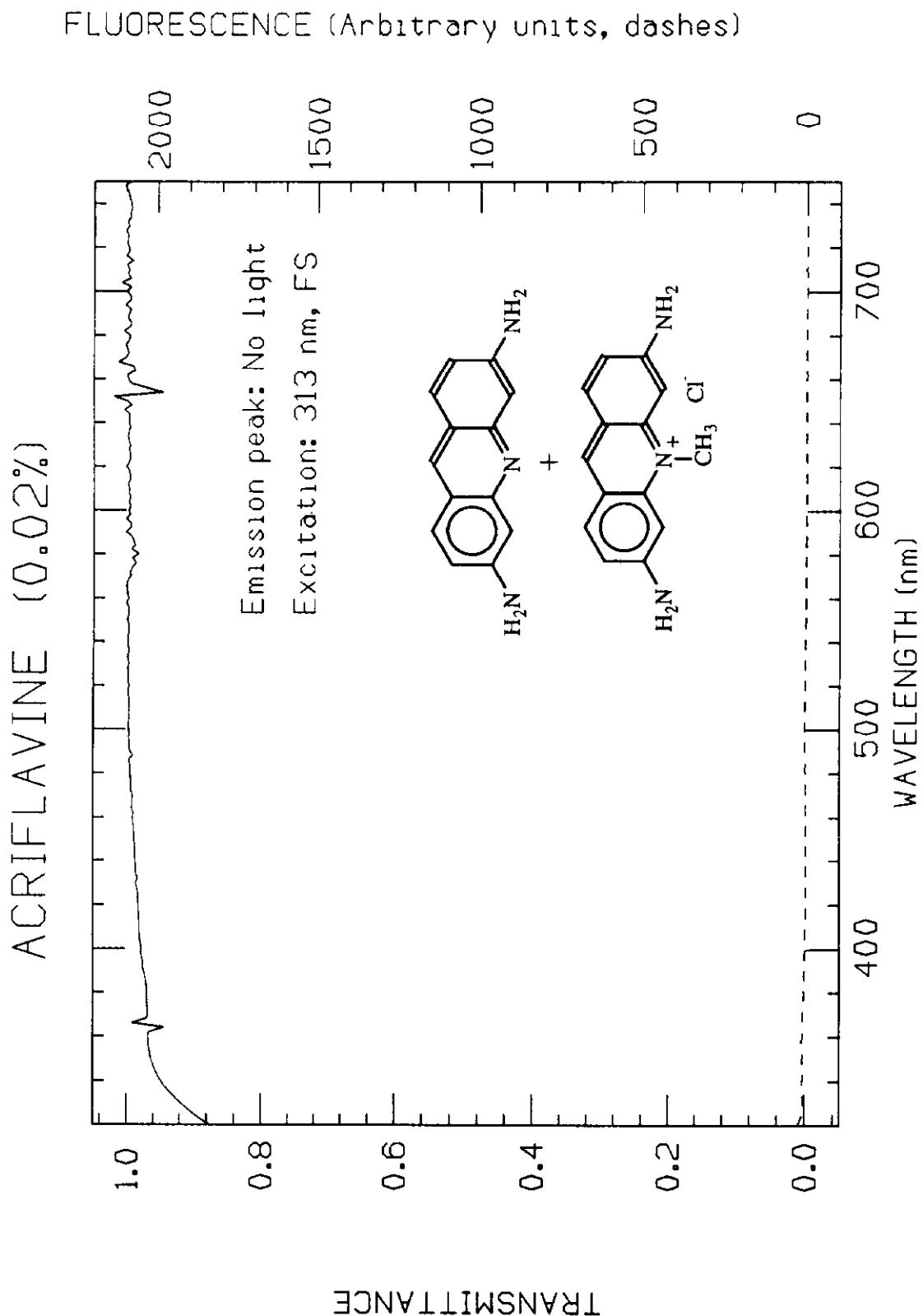
full names and the Chemical Abstracts Service (CAS) registry numbers for all the dopants tested. The CAS numbers are often listed in catalogs and handbooks next to the commercial name of the substance. Usually Material Safety Data Sheets provided by the vendors also contain some of this basic information. The chemical structures were drawn or searched once the full names or CAS numbers were available. The chemical structure of the dopant has been included in the transmittance plus fluorescence plot. Appendix B contains a summary of all the fluorescence measurements performed. It also lists both the polymerization and radiation damage set numbers for further reference. The raw data from these irradiations will be provided in another document. Appendix C displays a table with the spectroscopic data currently available. Further details in the light yield (brightness) measurements, the lifetime determinations and their setup will be published.

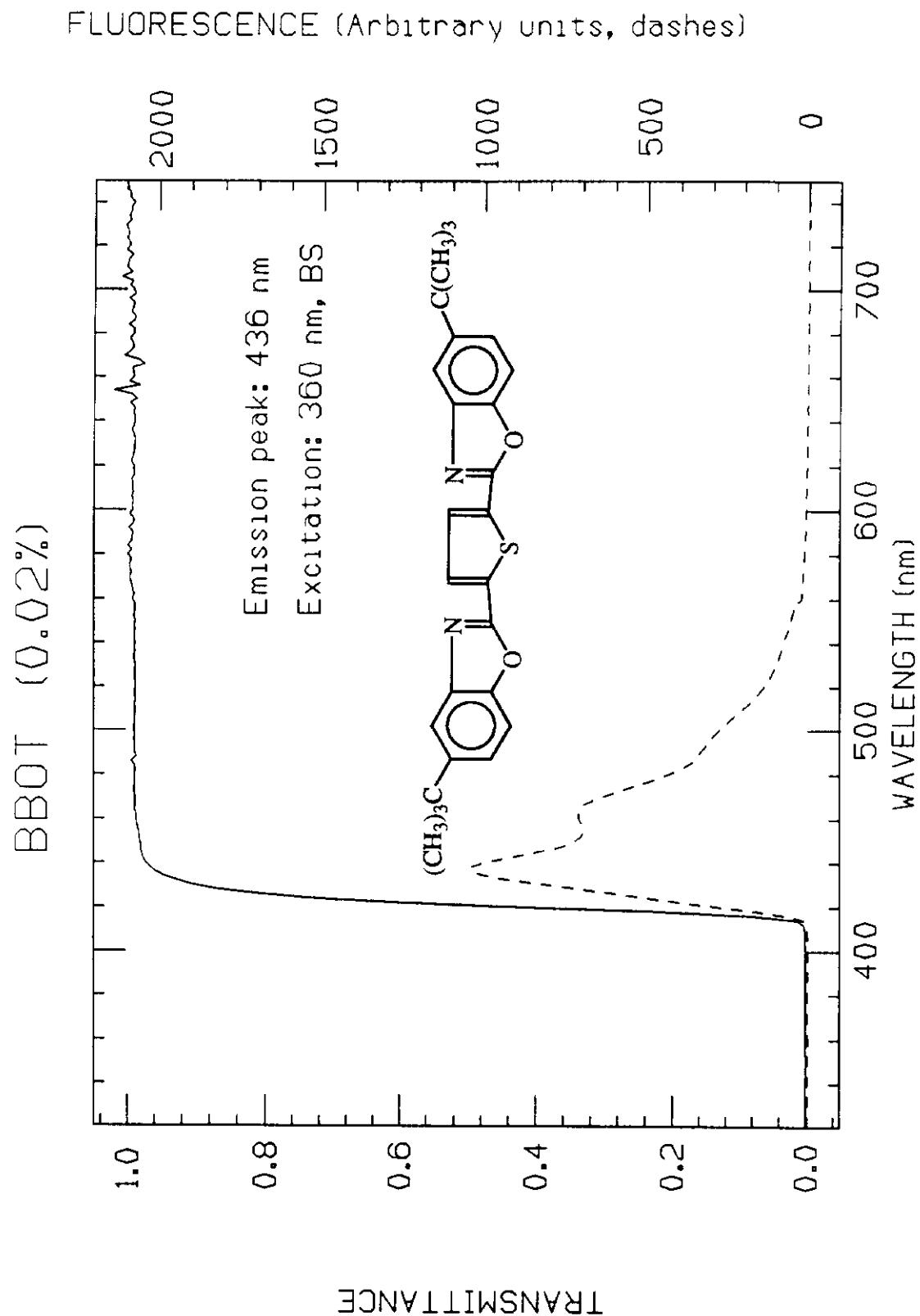
We wish to thank the members of the Particle Detector Group for their help and advice; in particular, Monica Szelag whose plotting skills and good humor became critical to the final outcome of these documents.

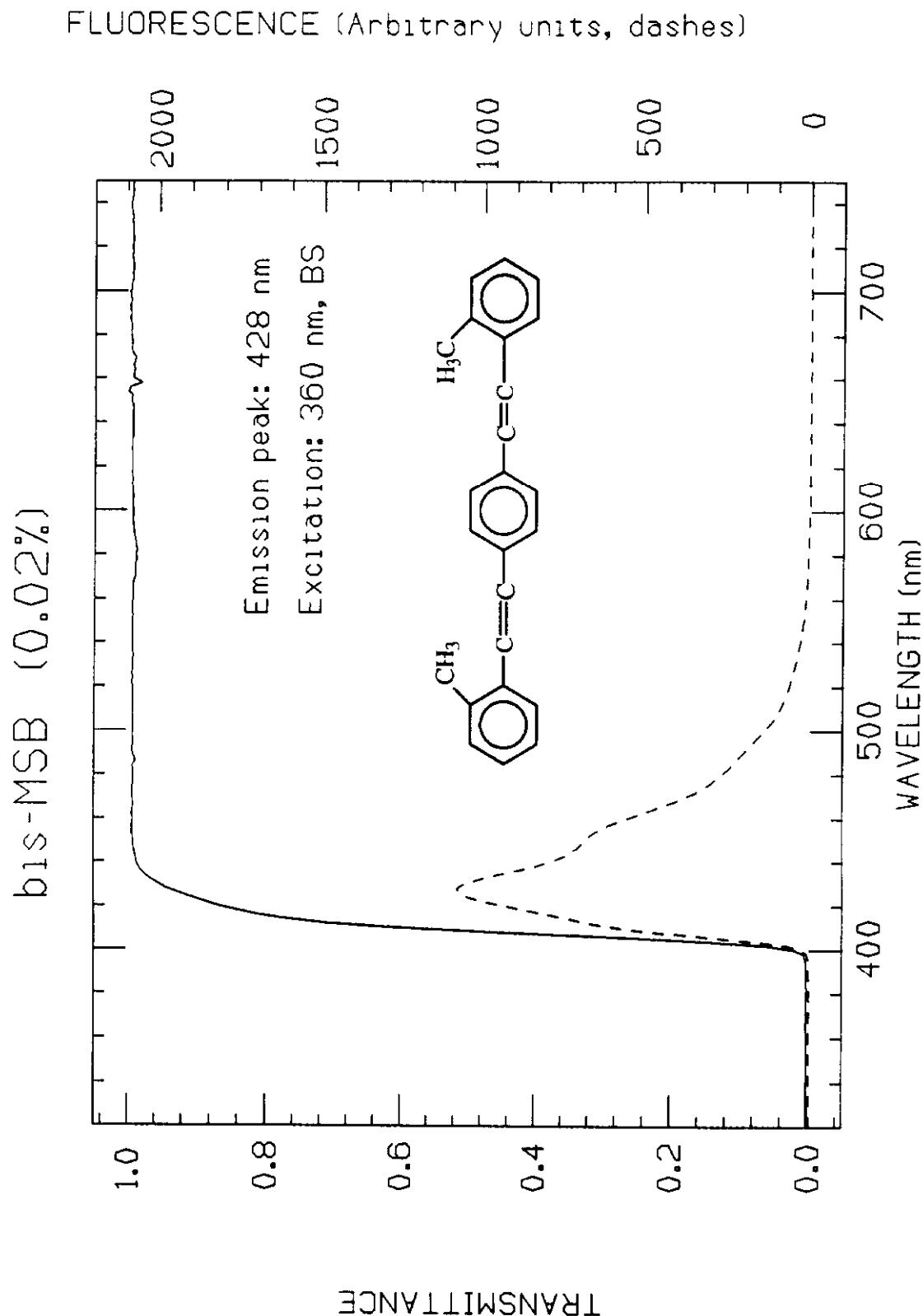


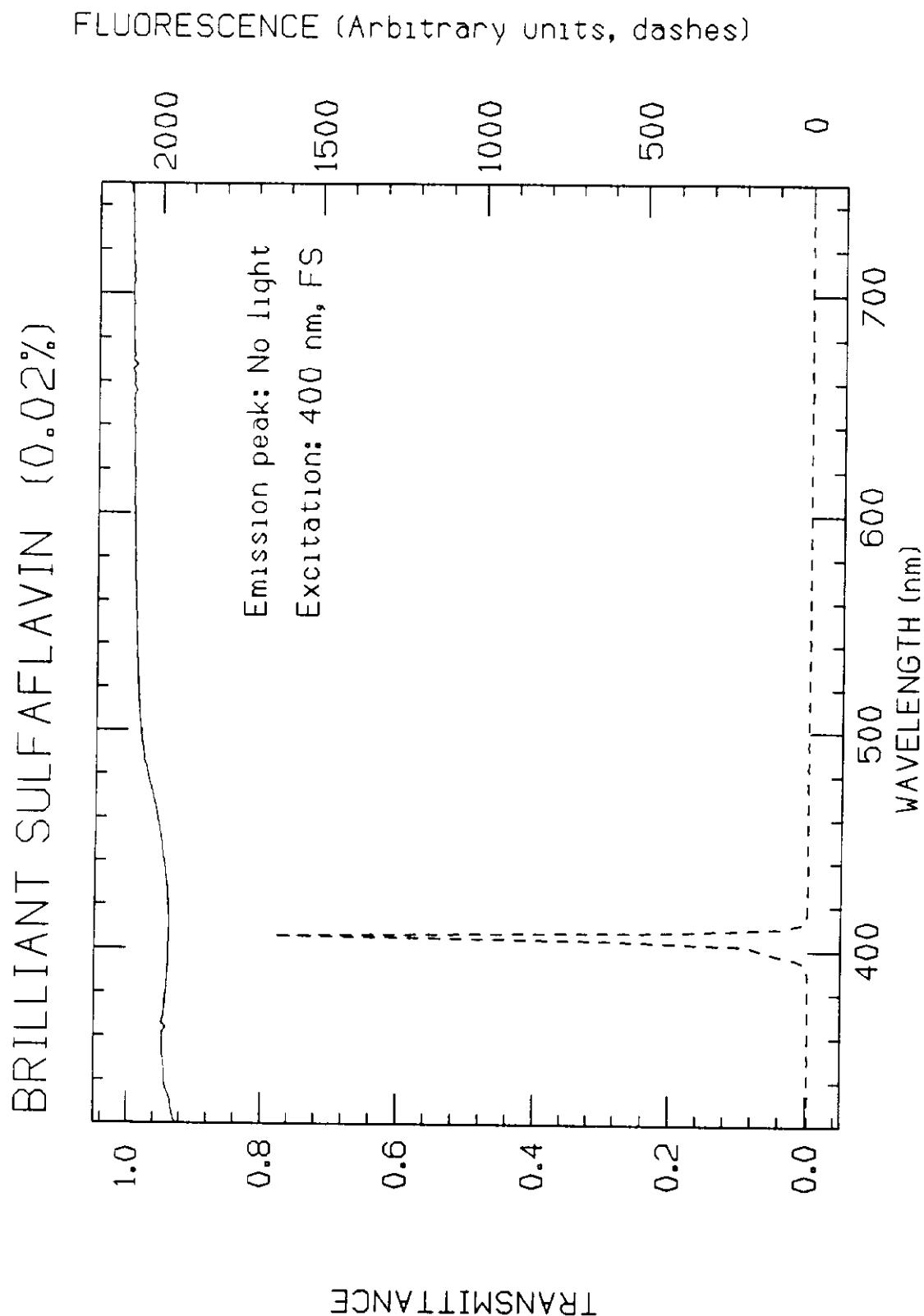


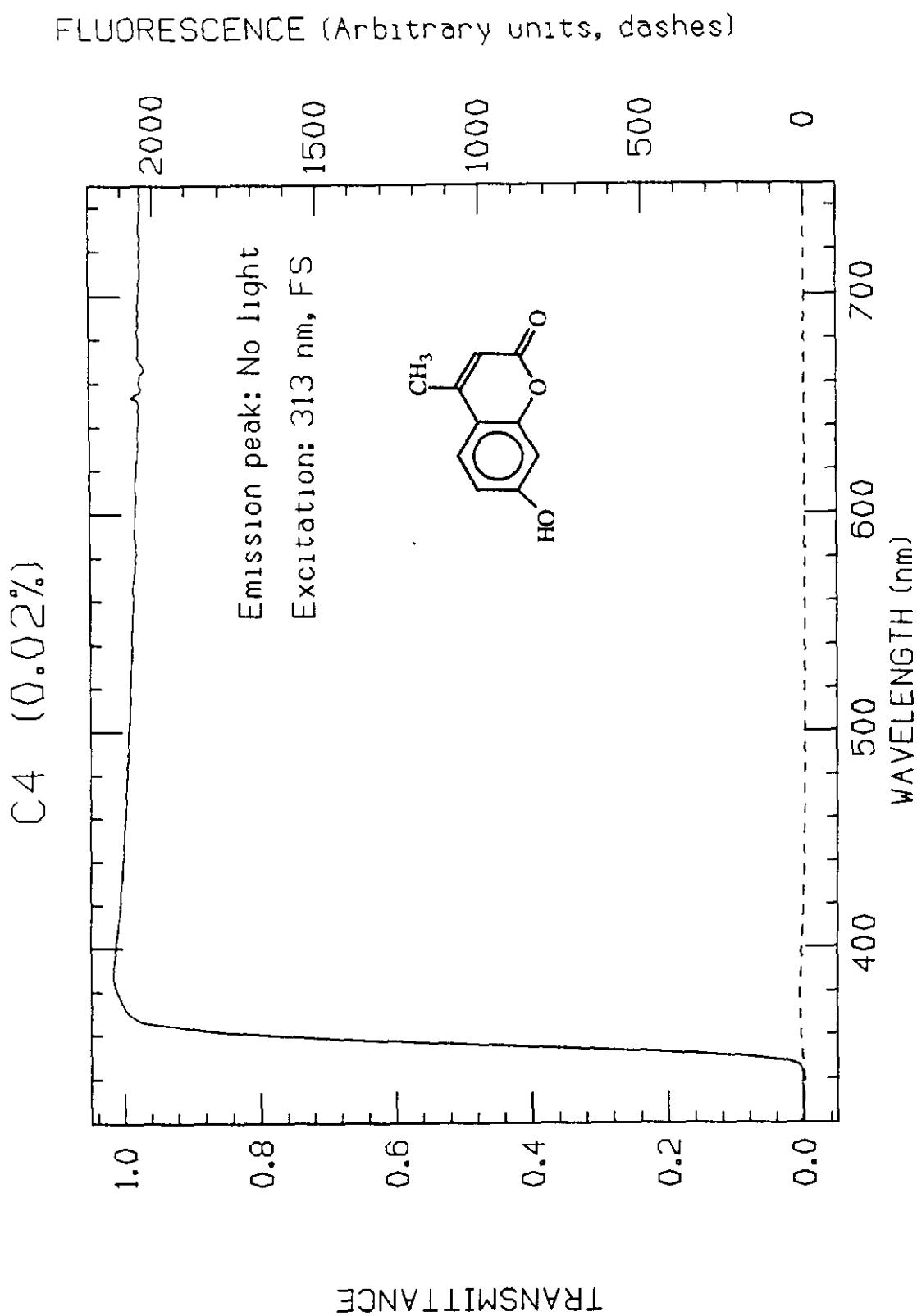


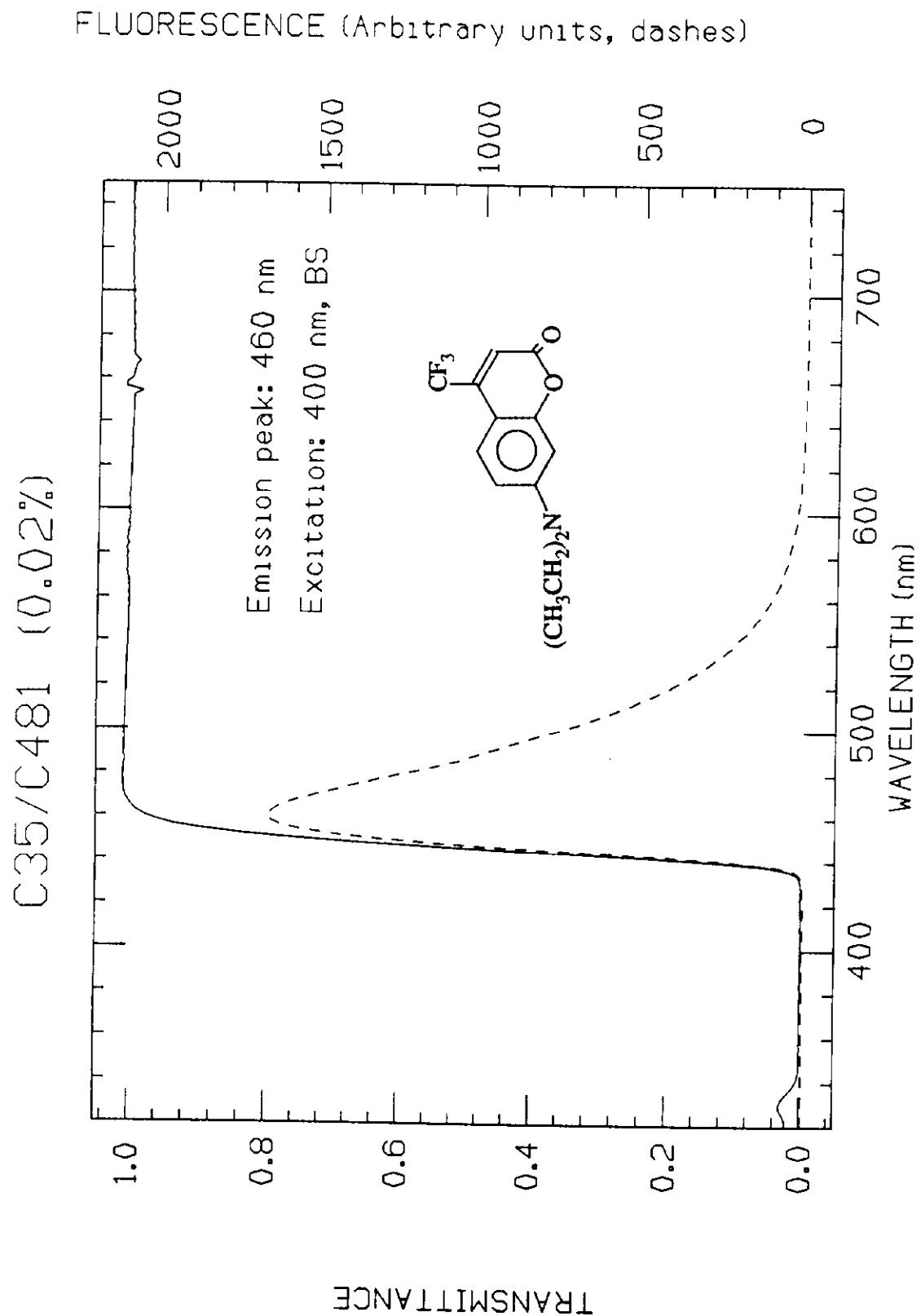


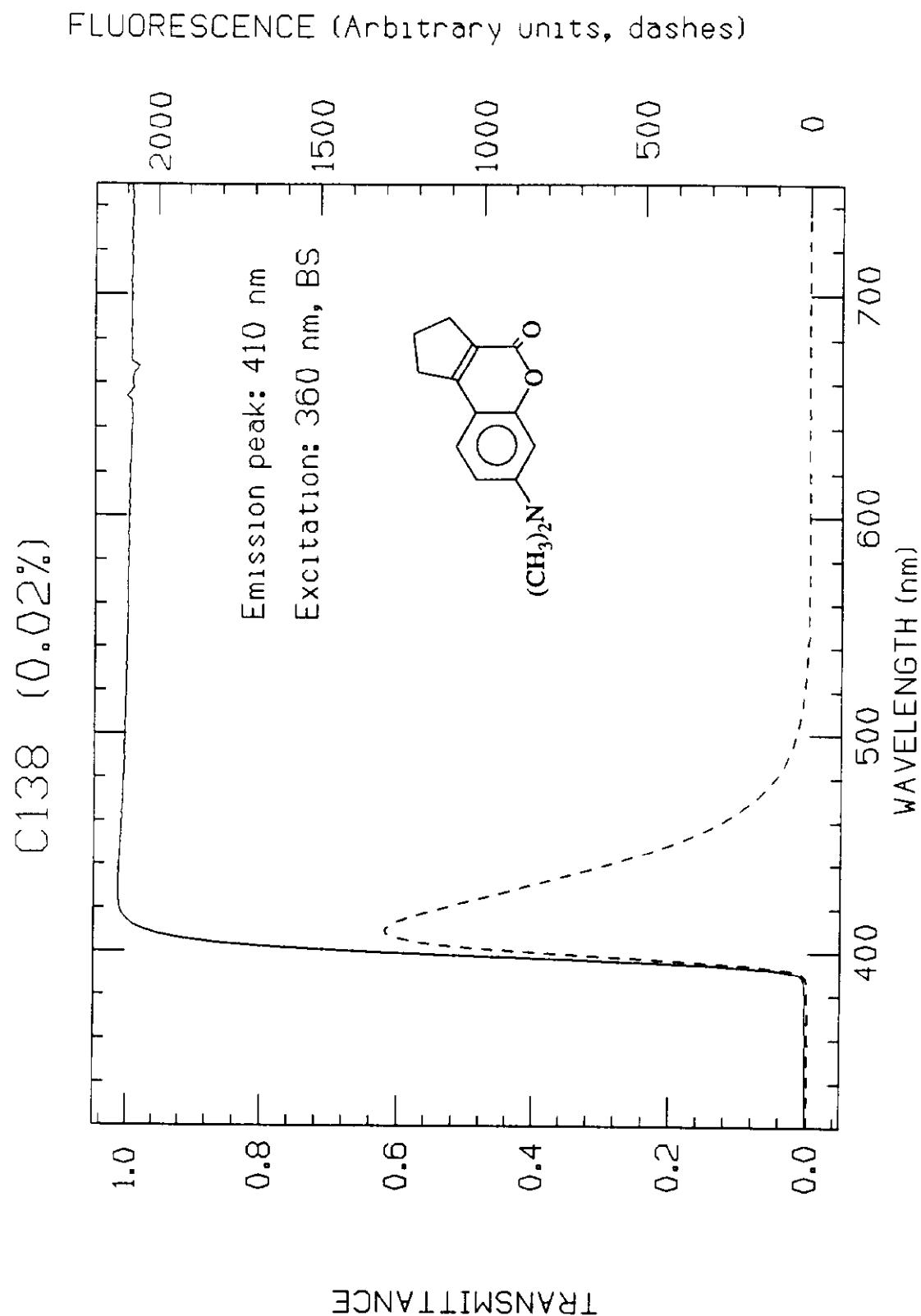


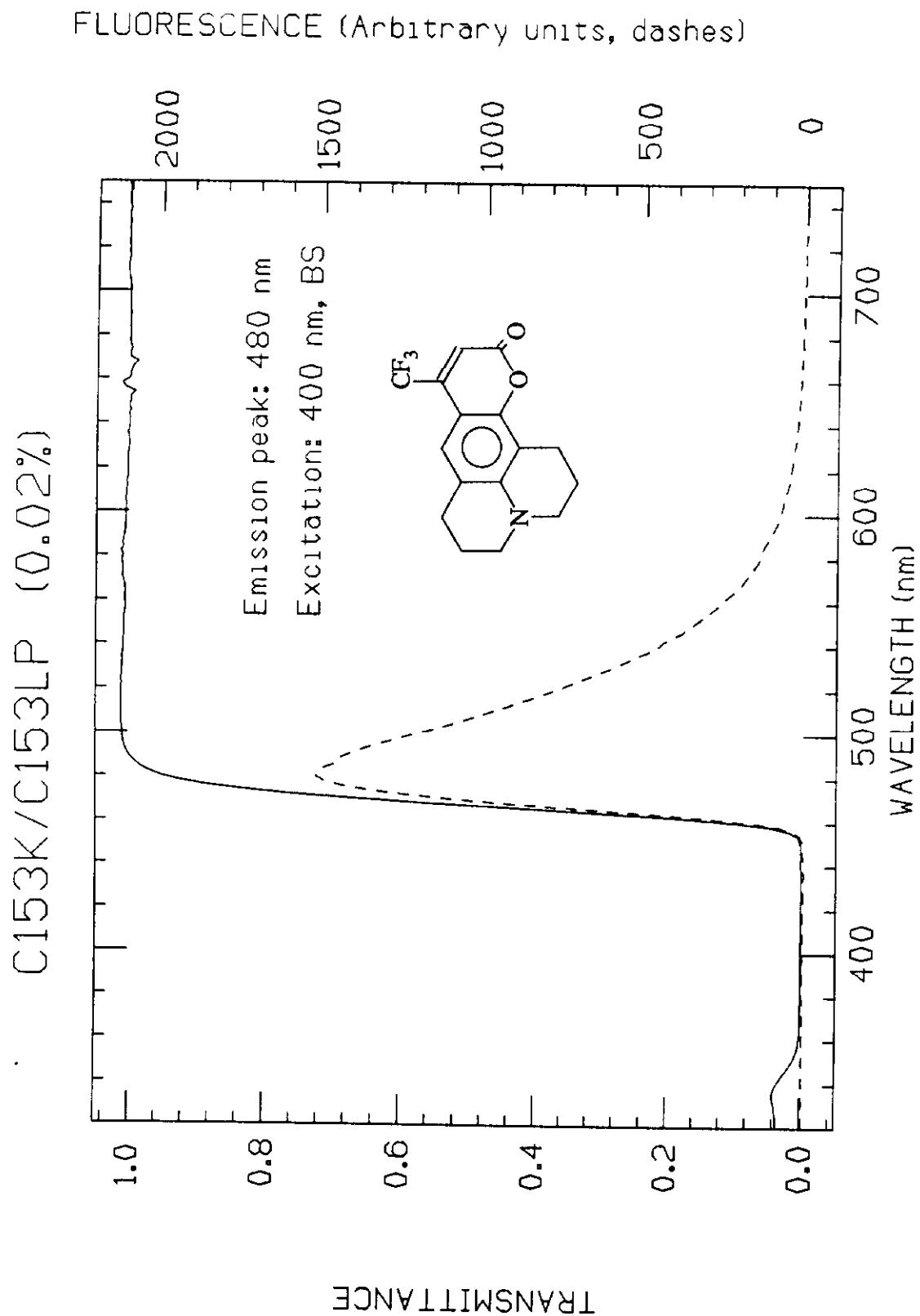


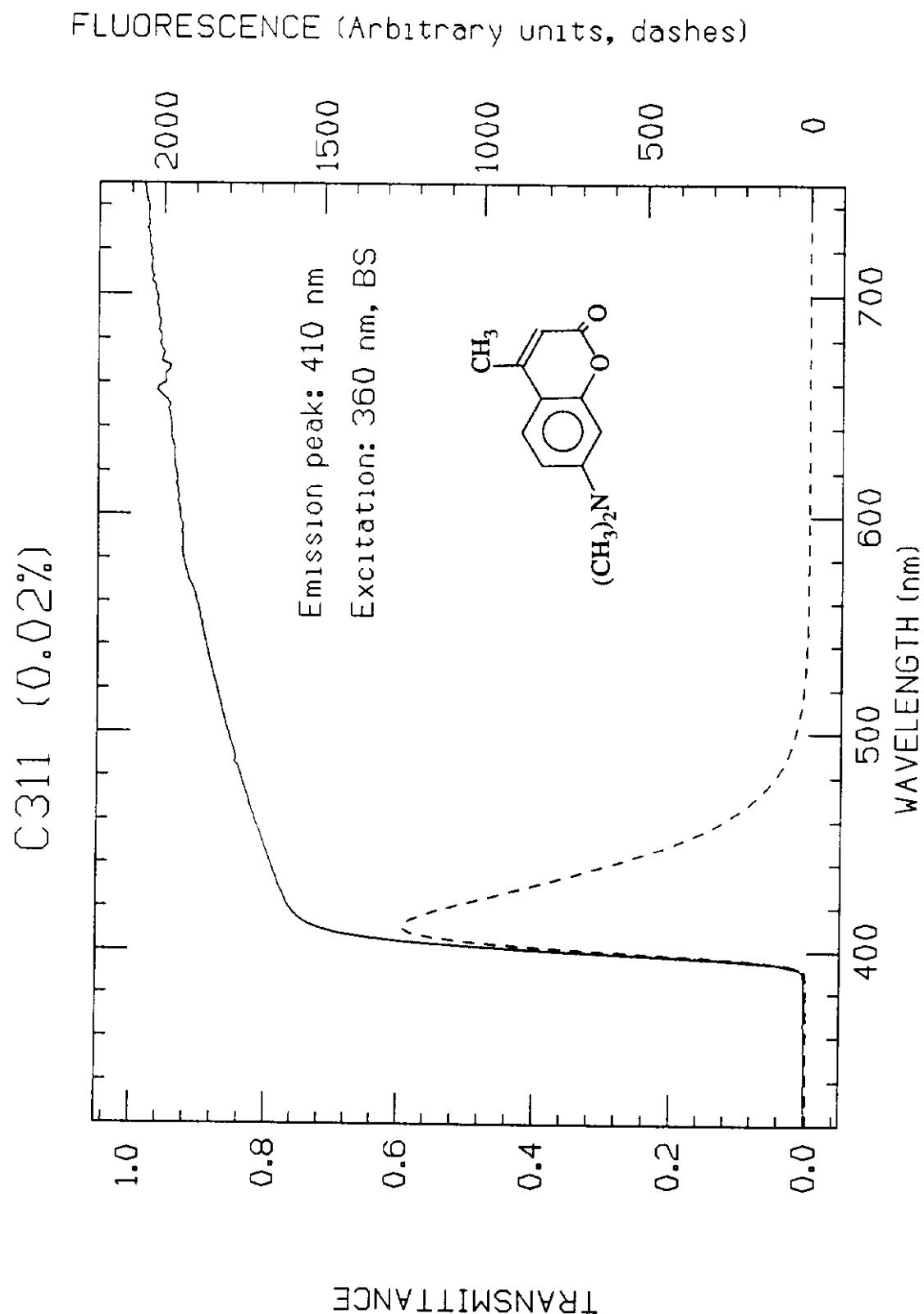


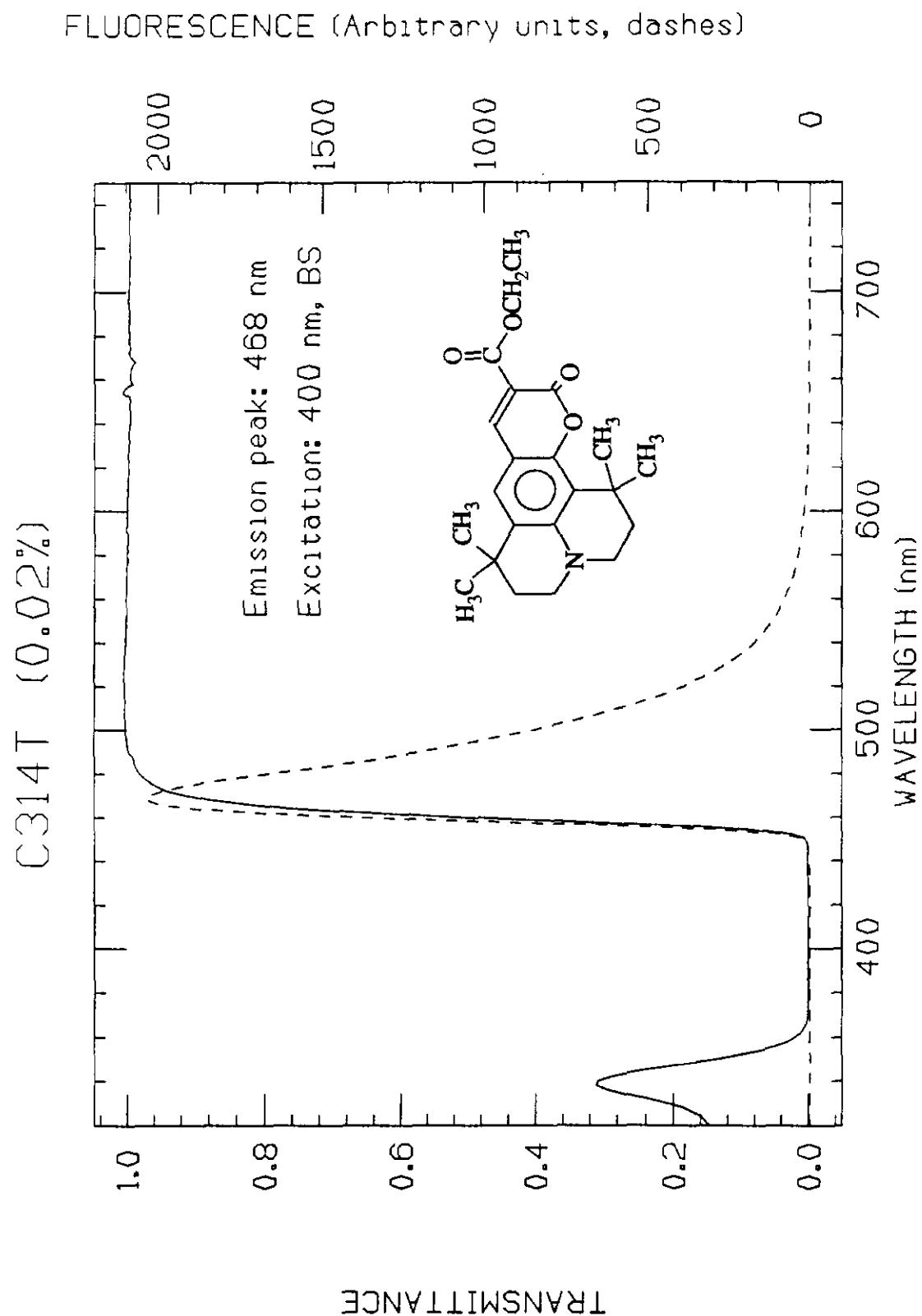


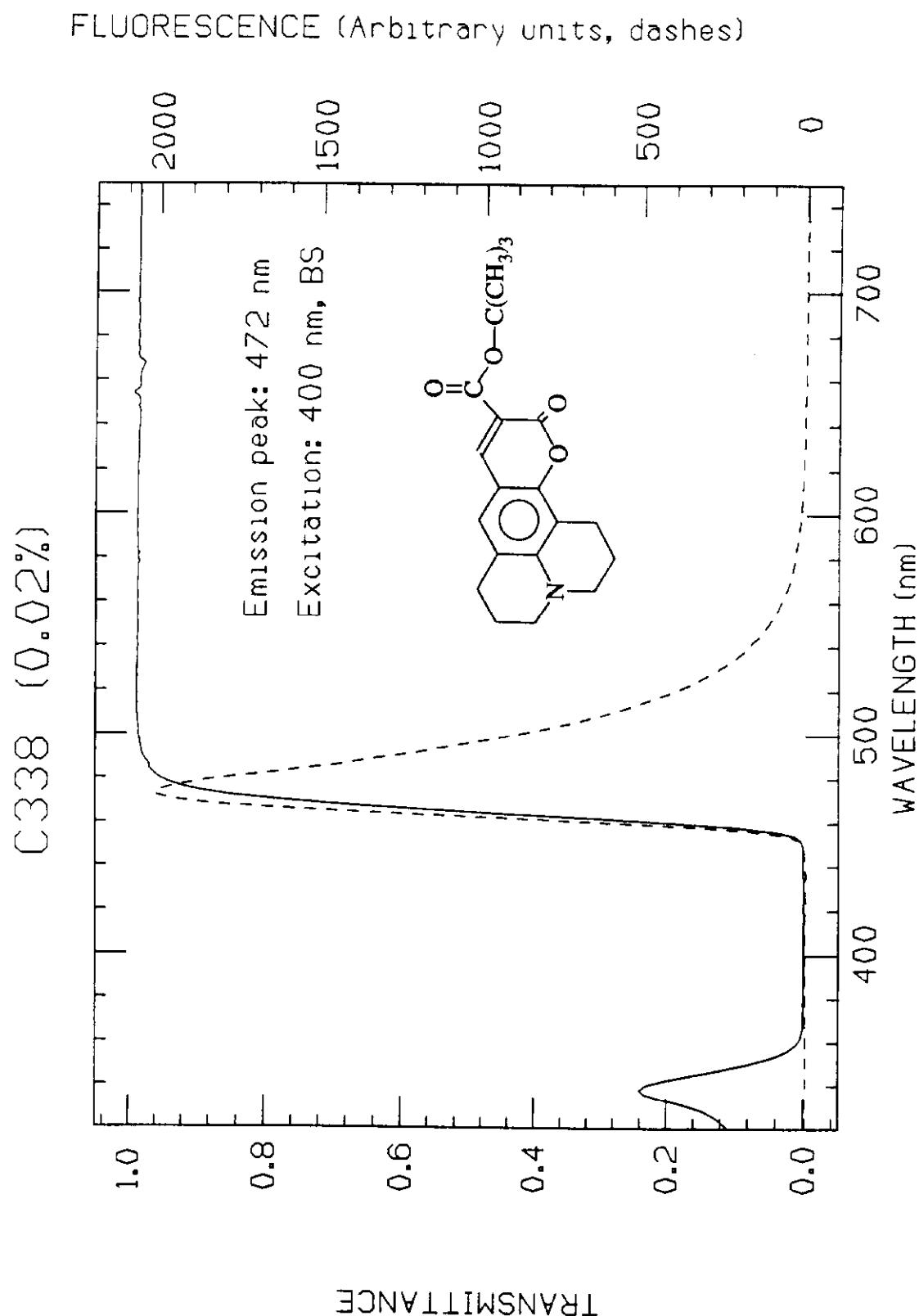


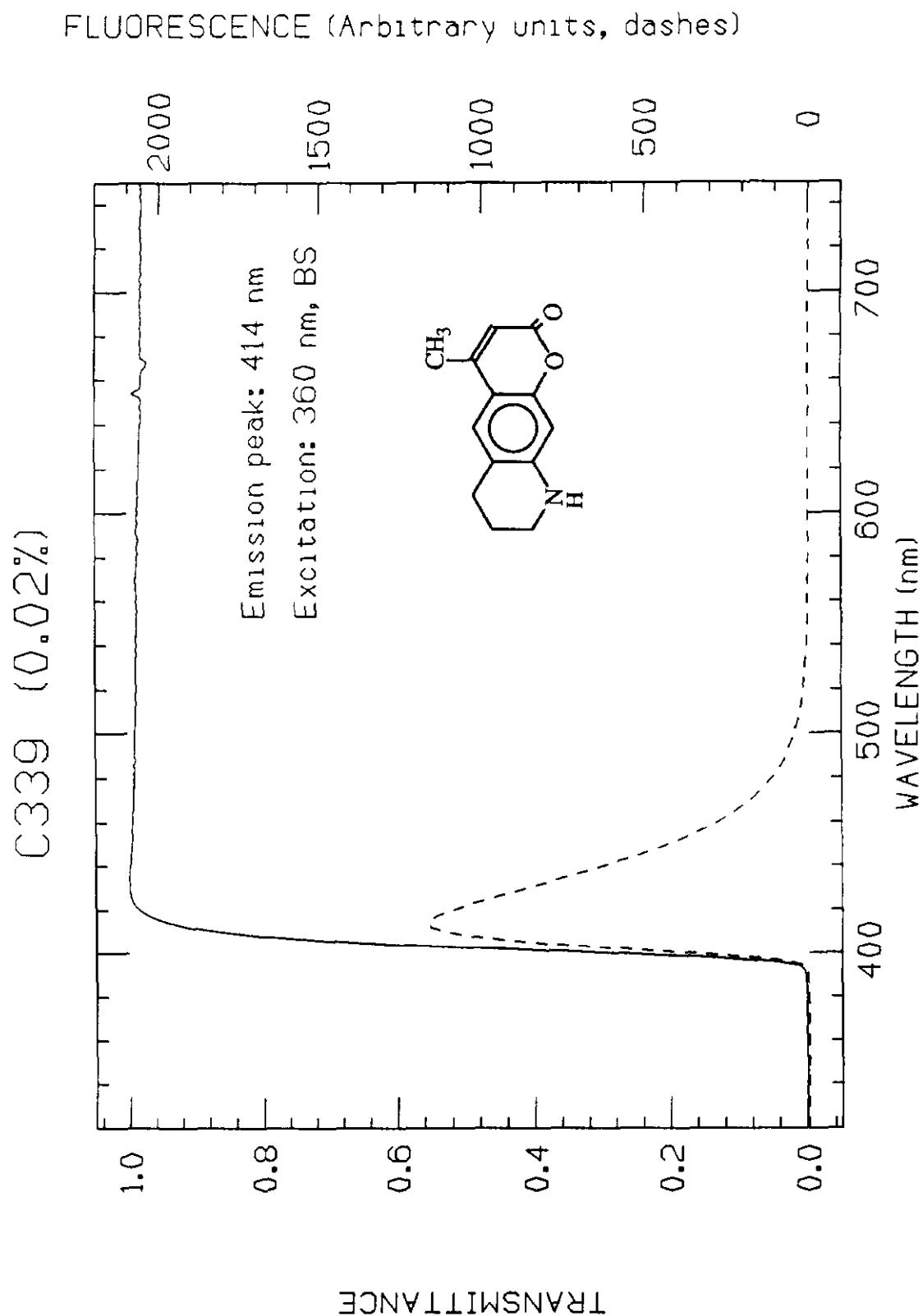


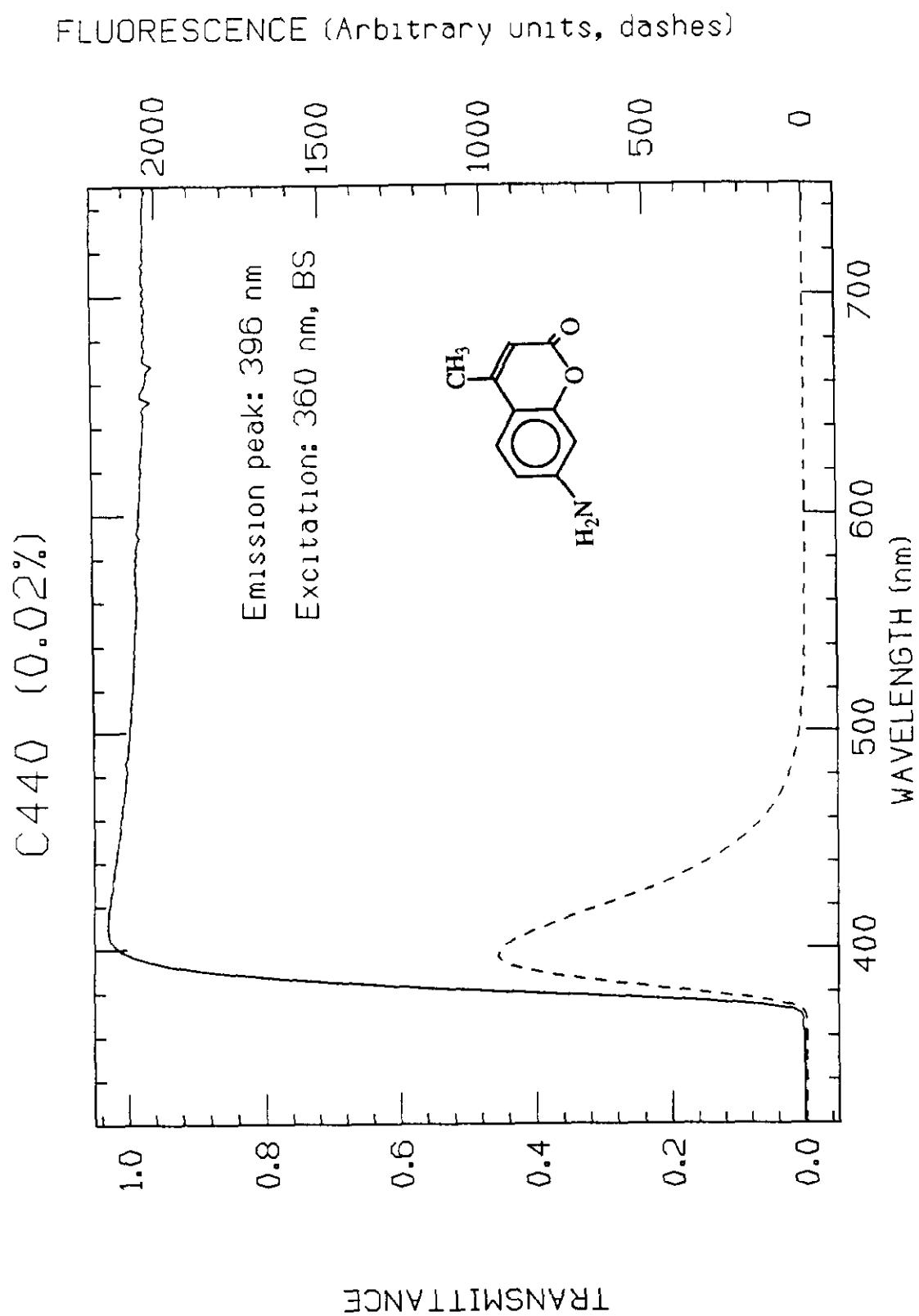


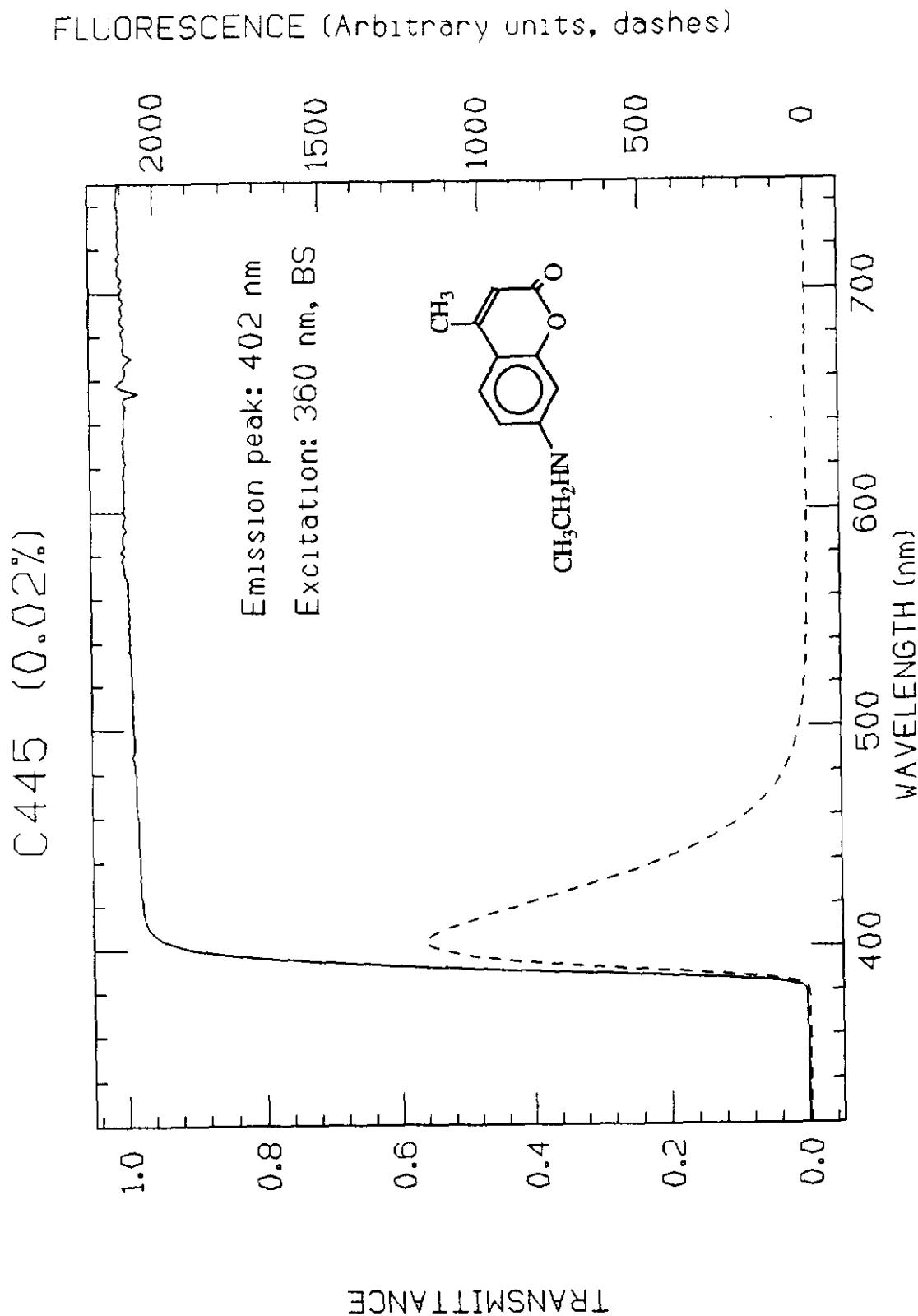


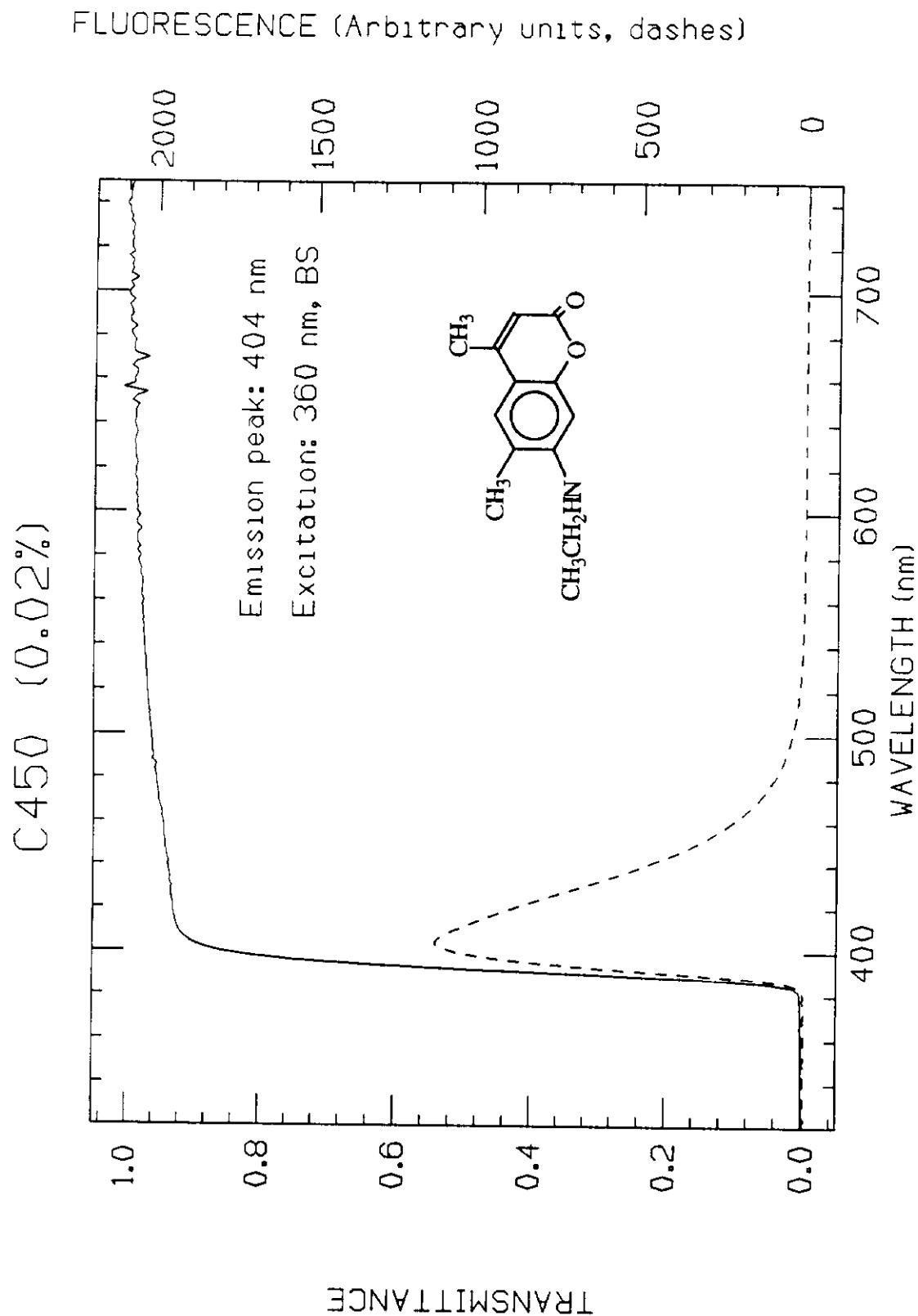


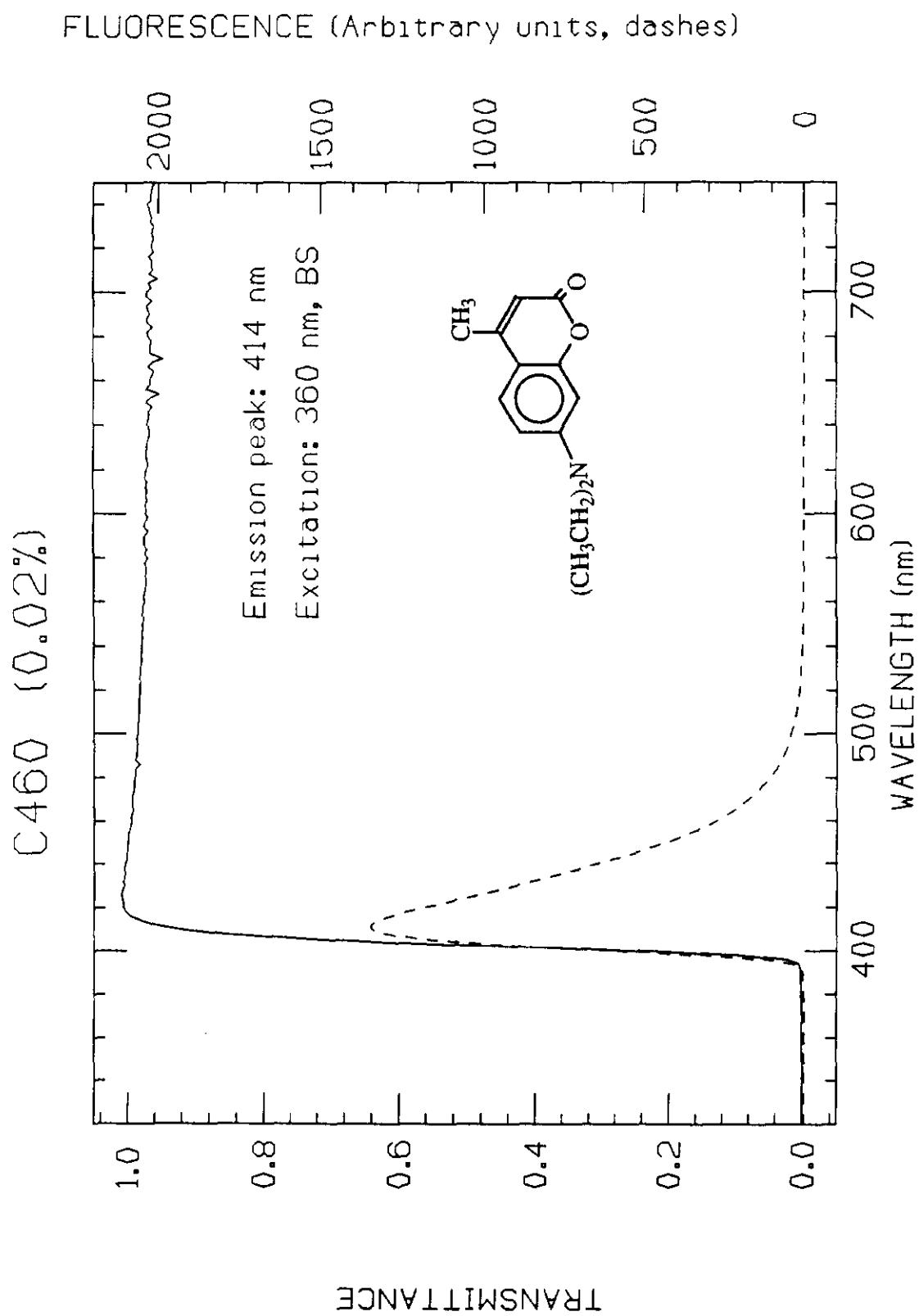


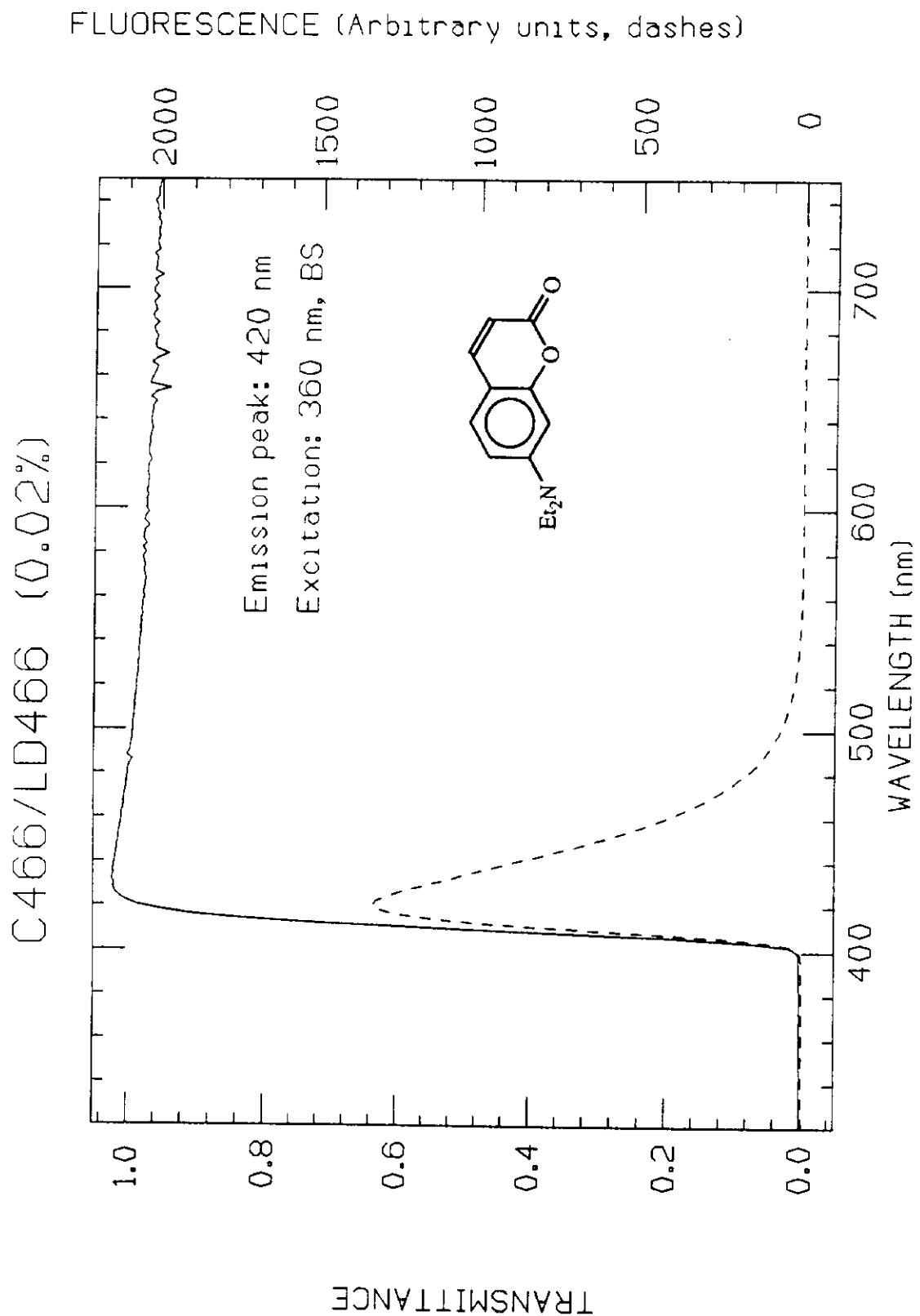


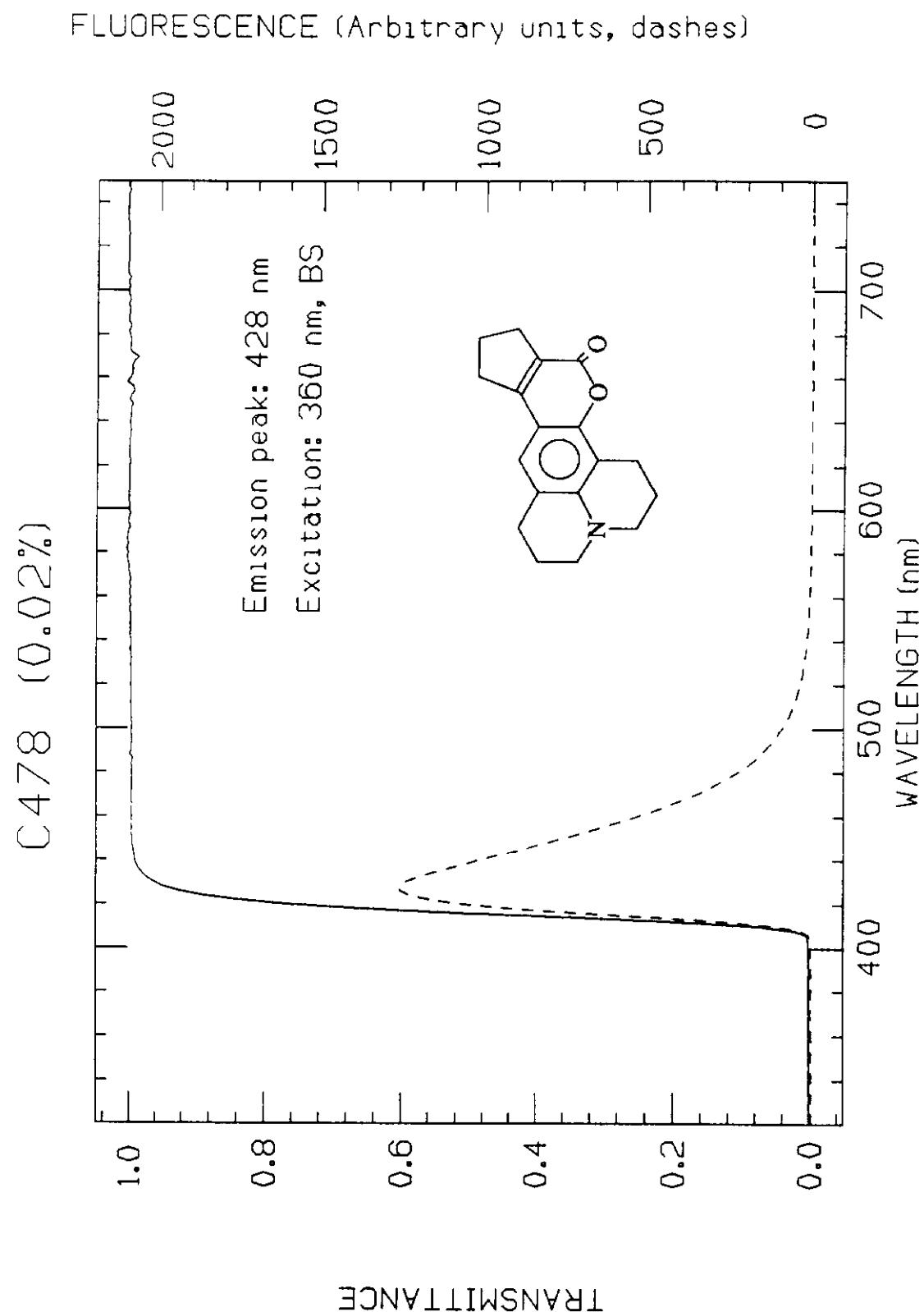


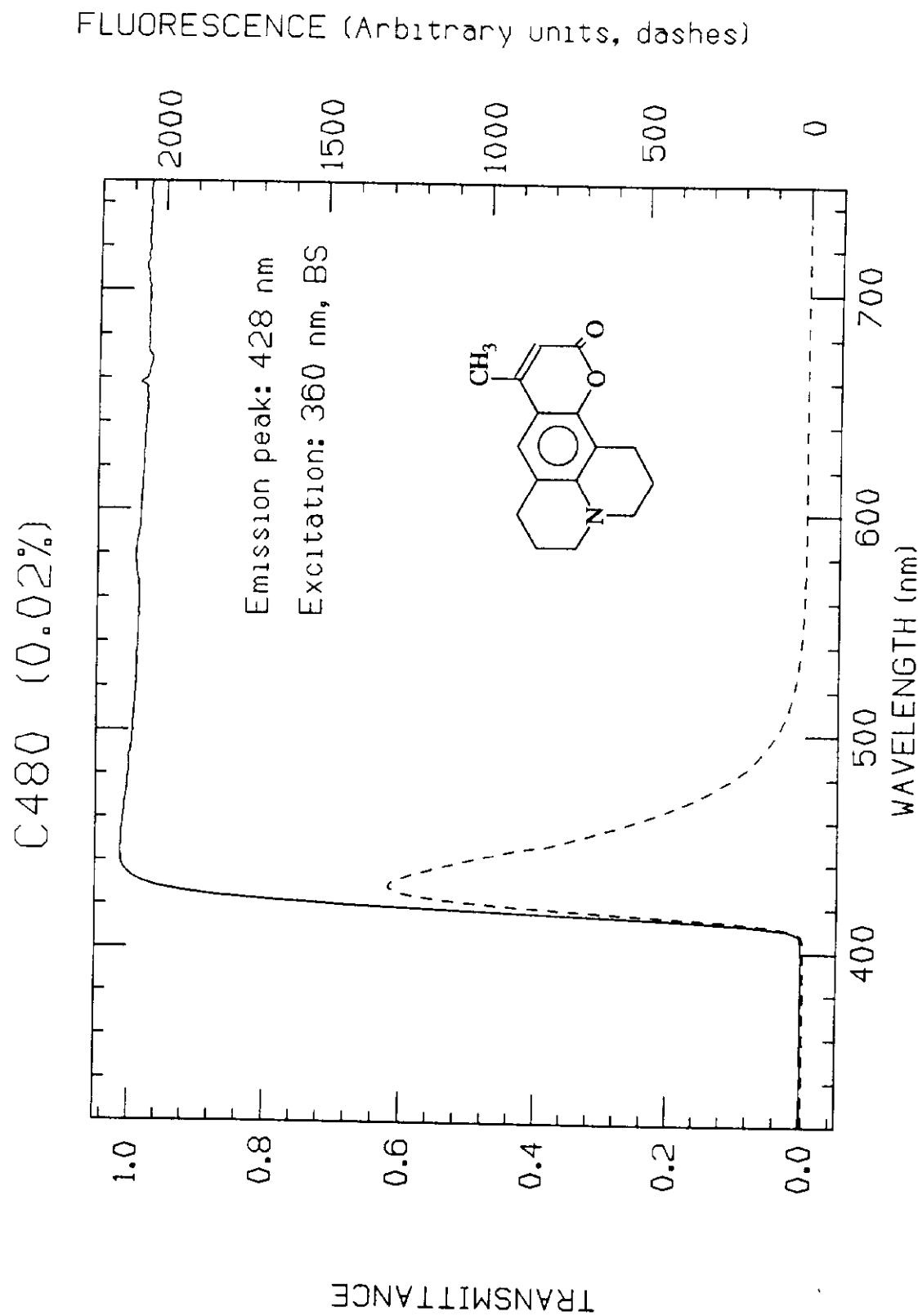


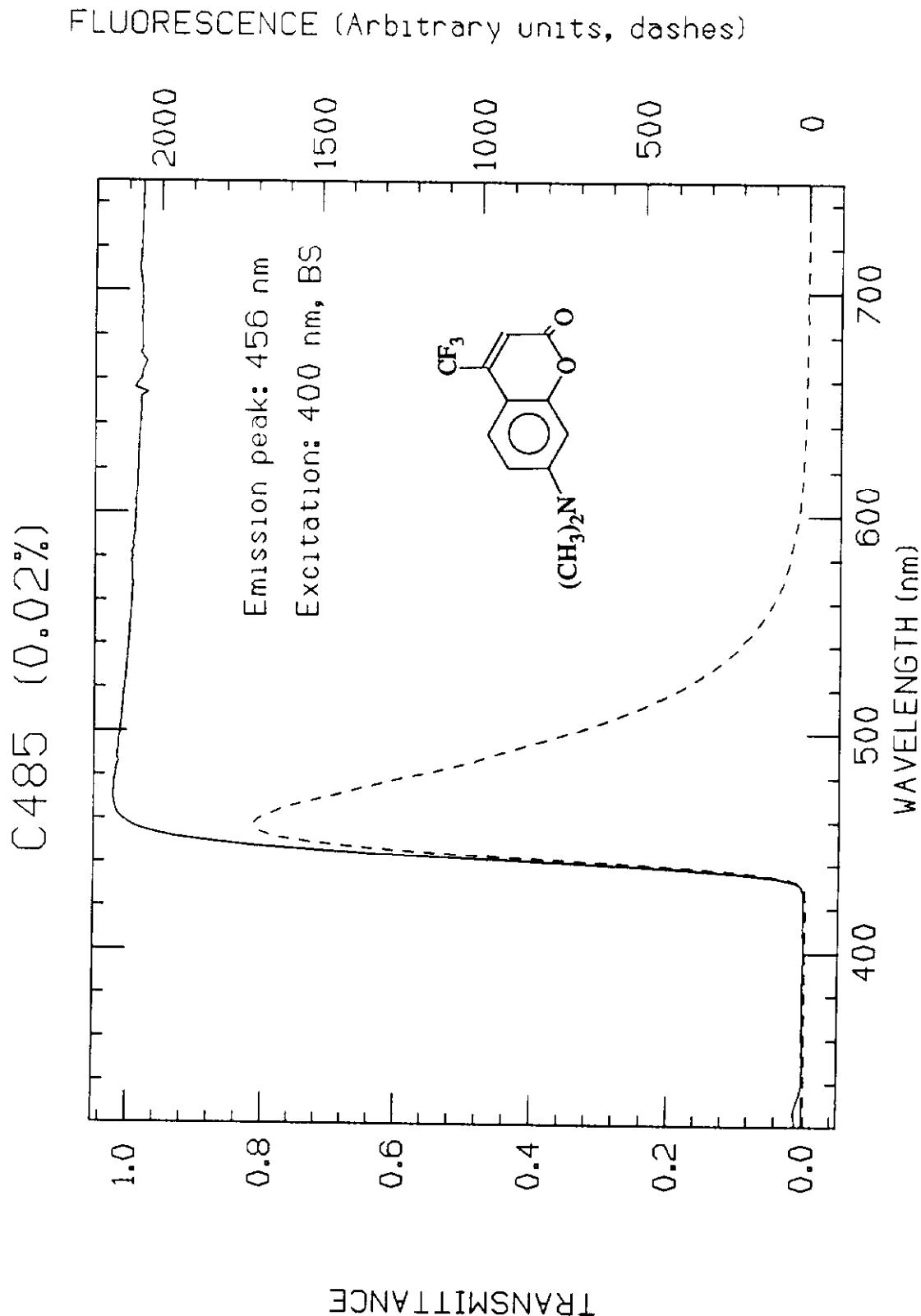


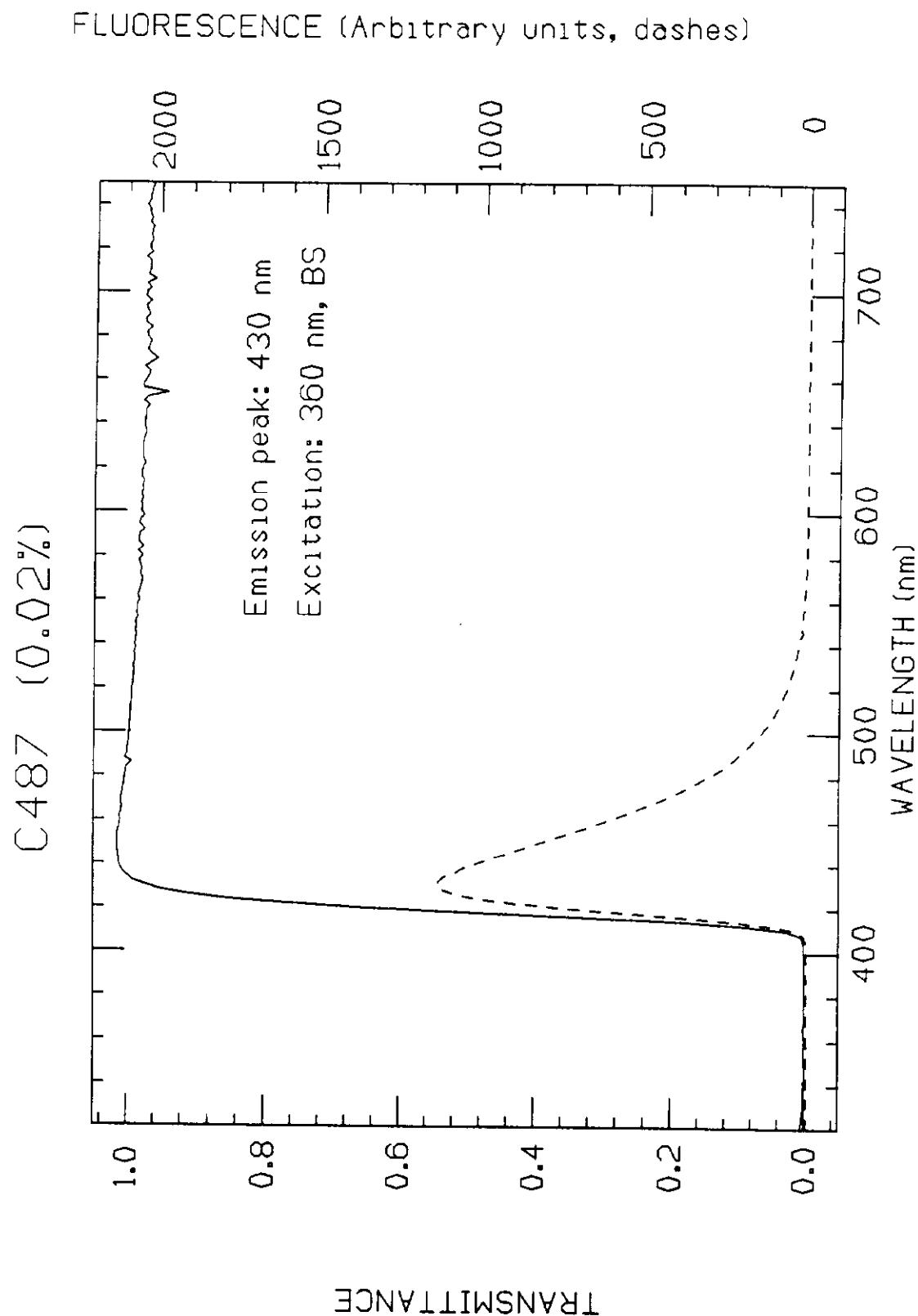


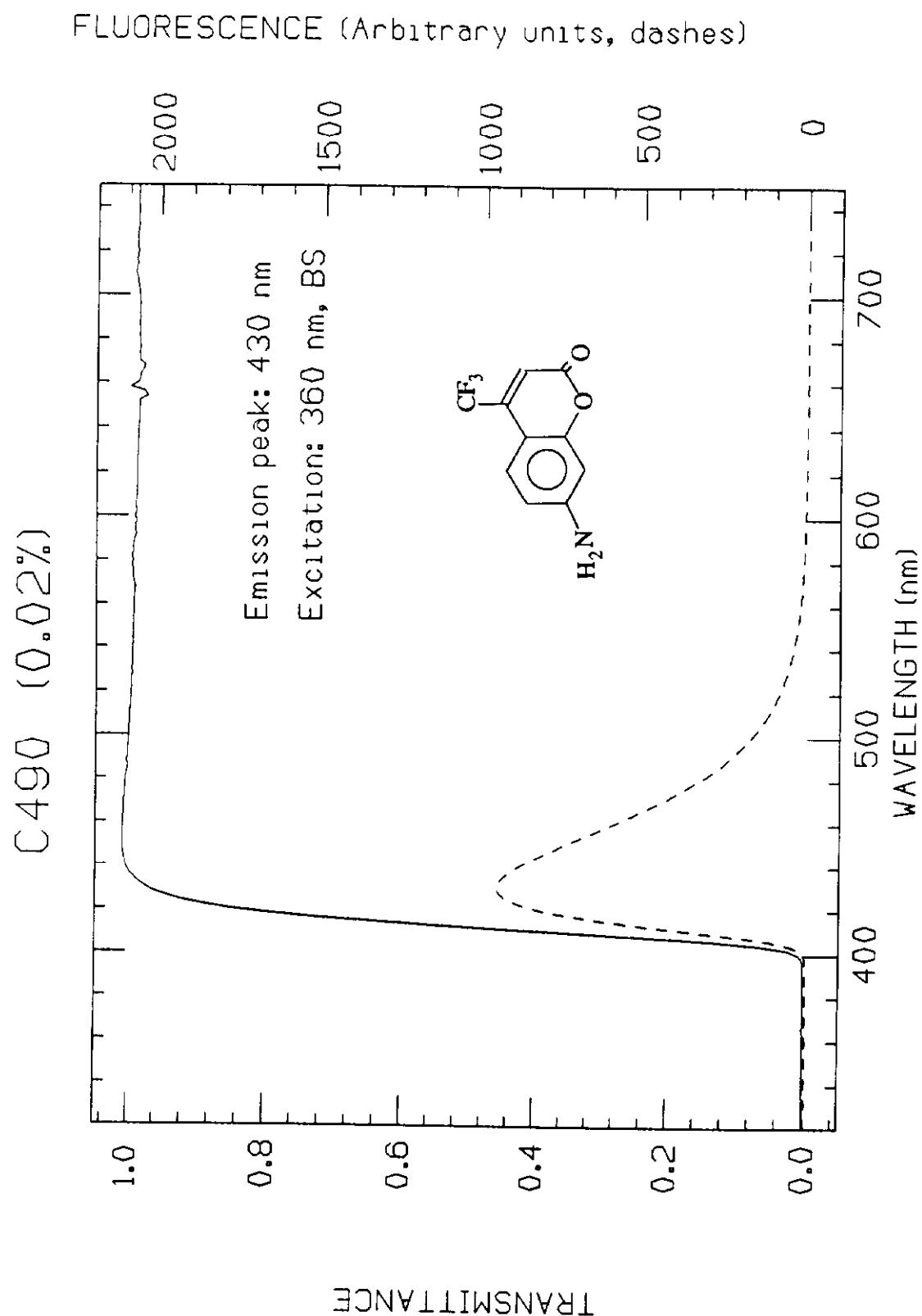


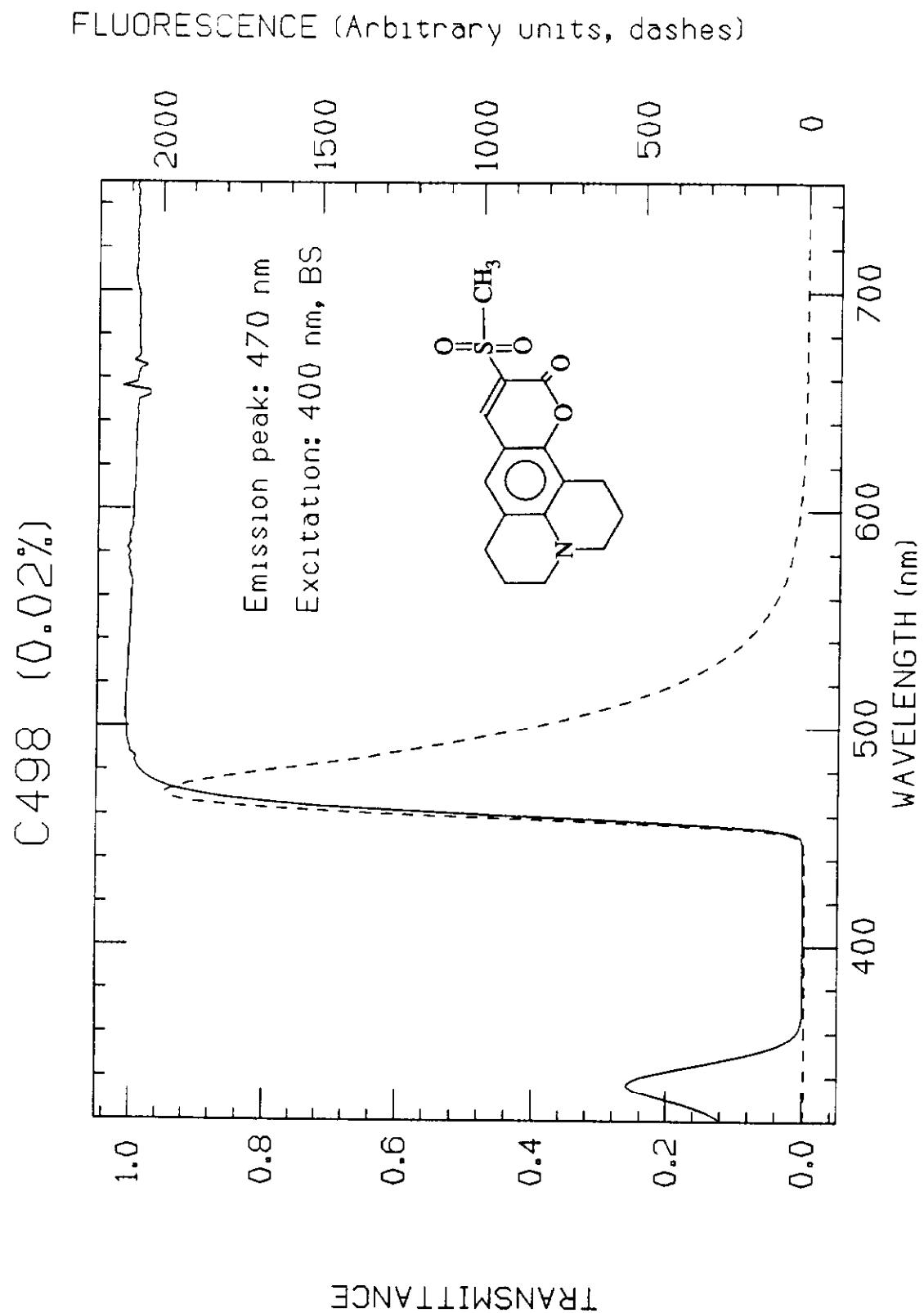


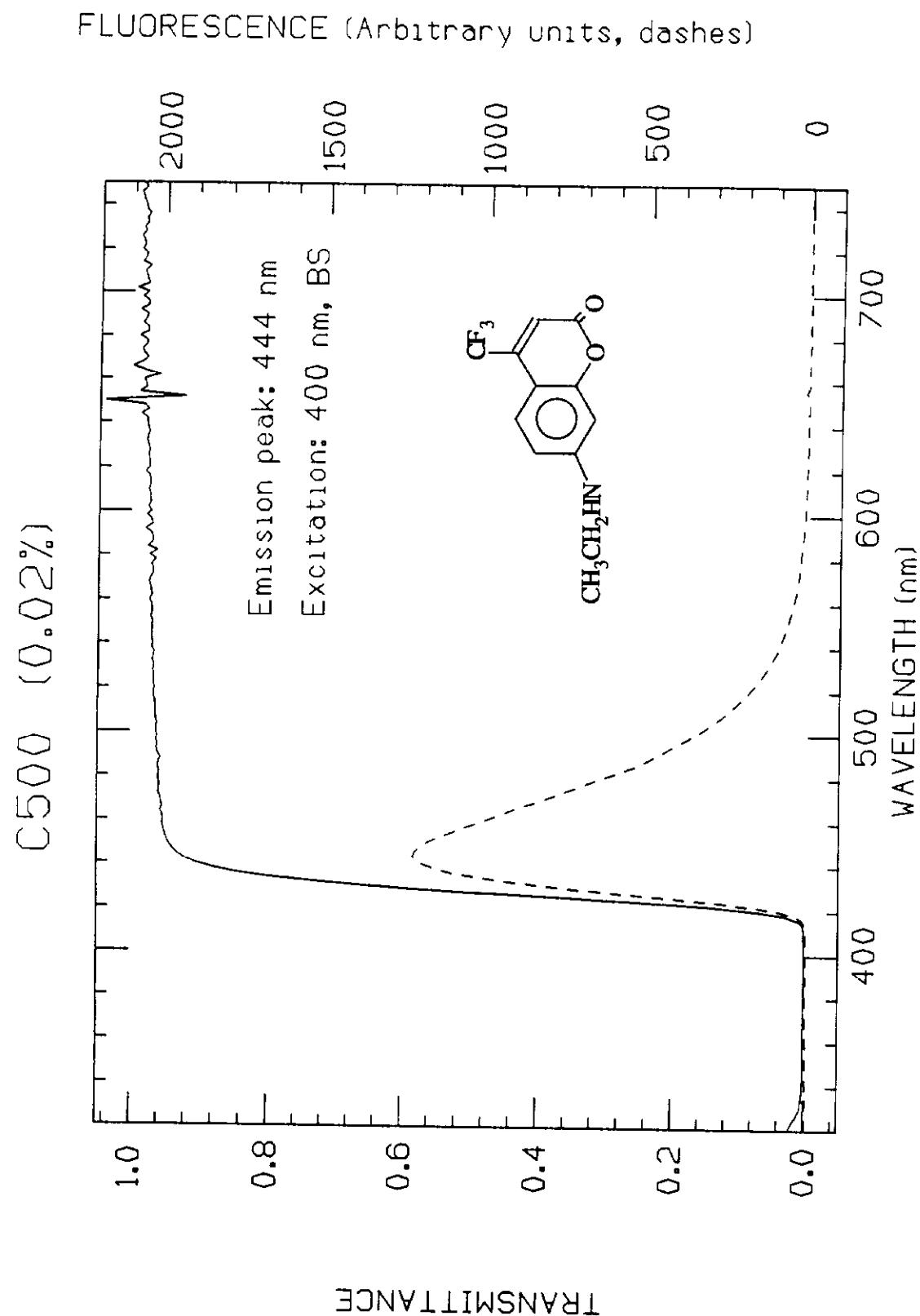


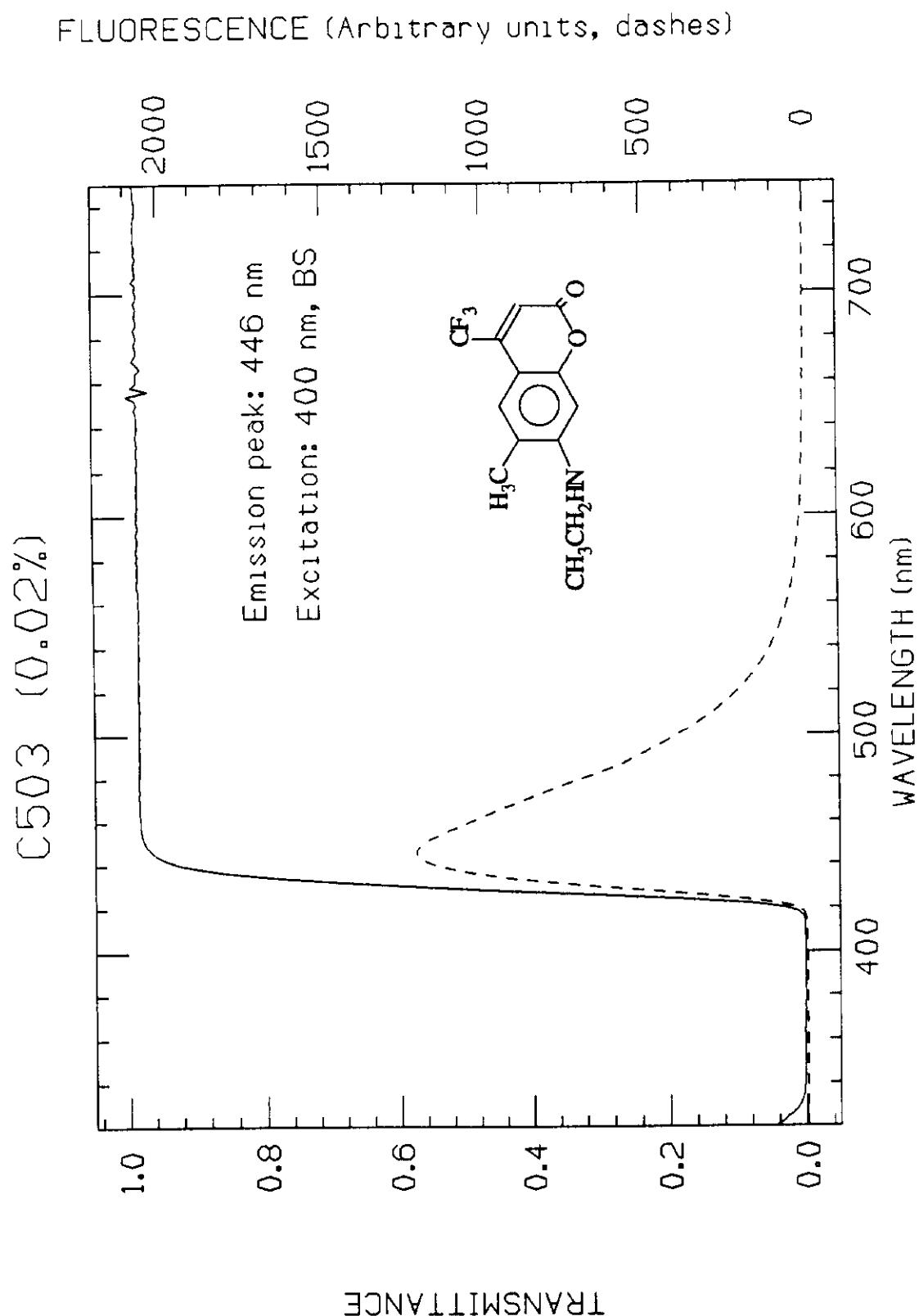


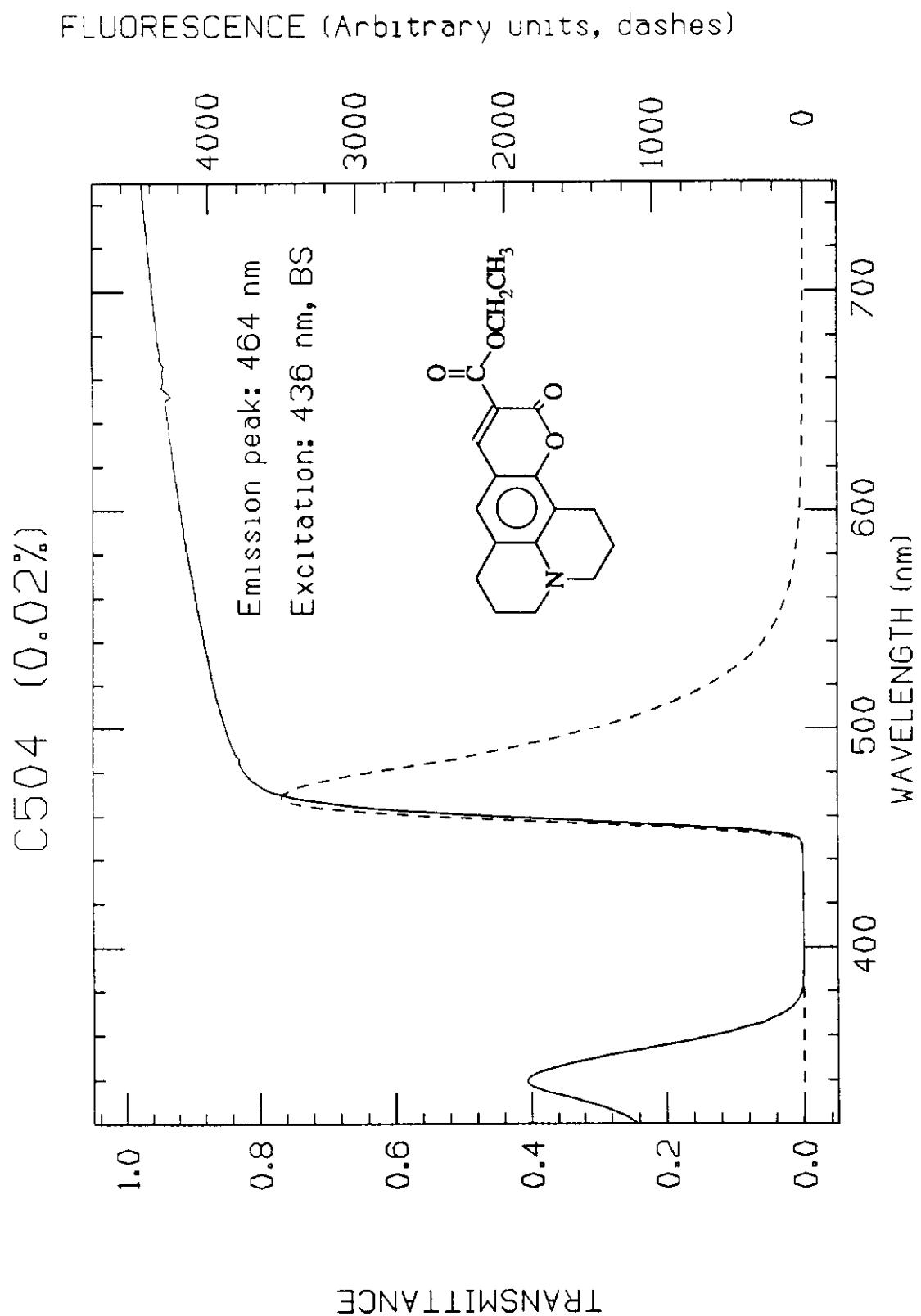


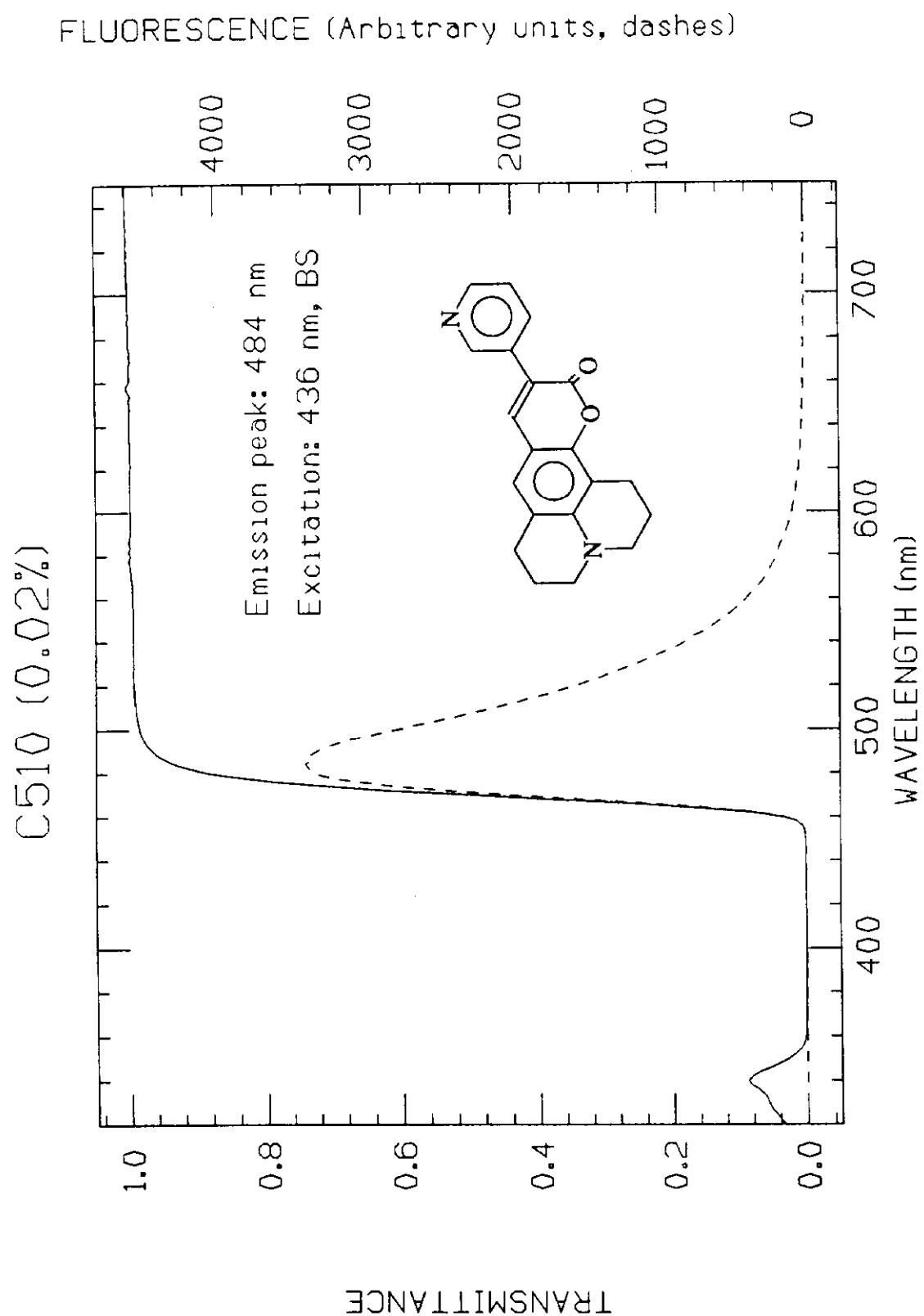


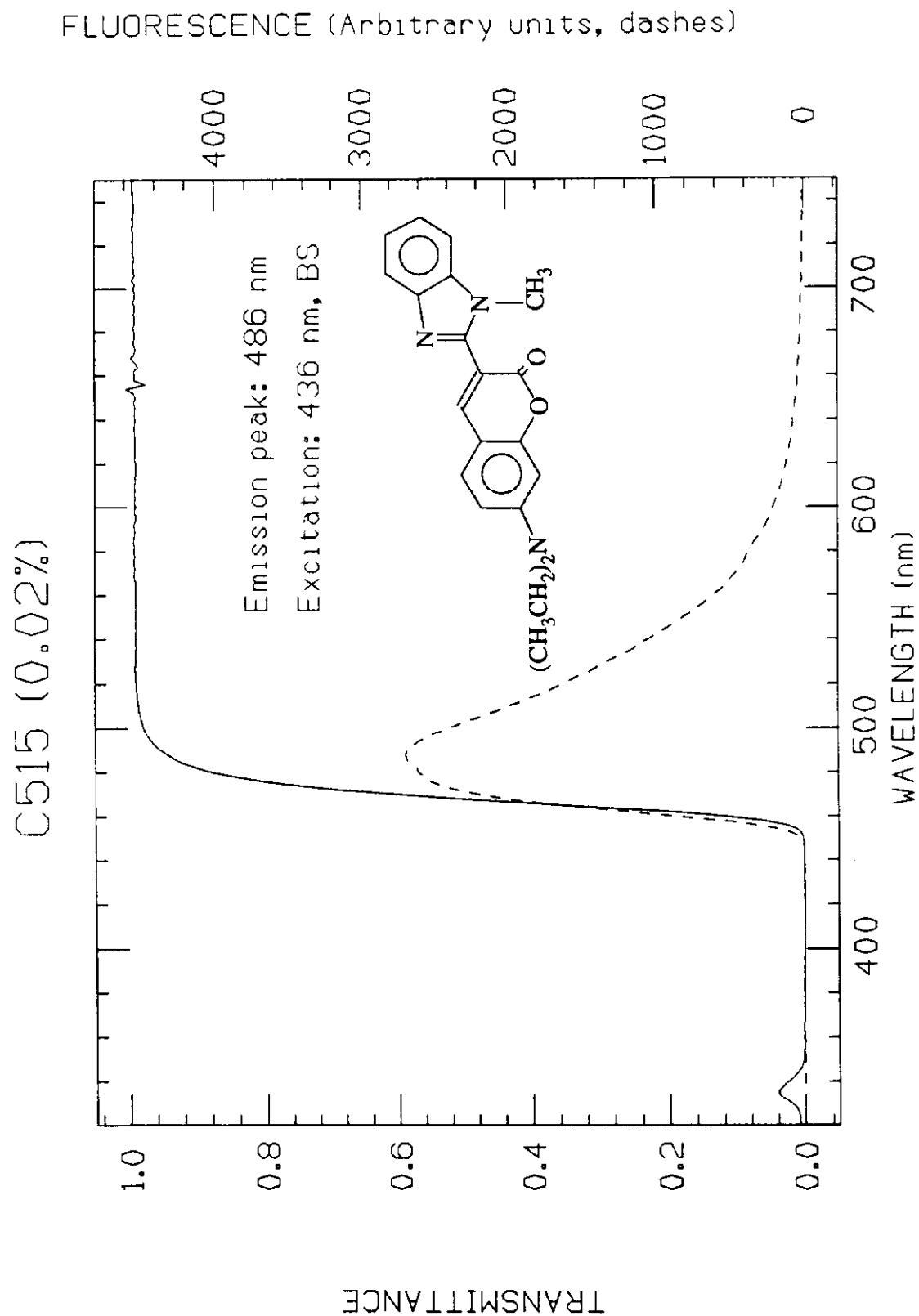


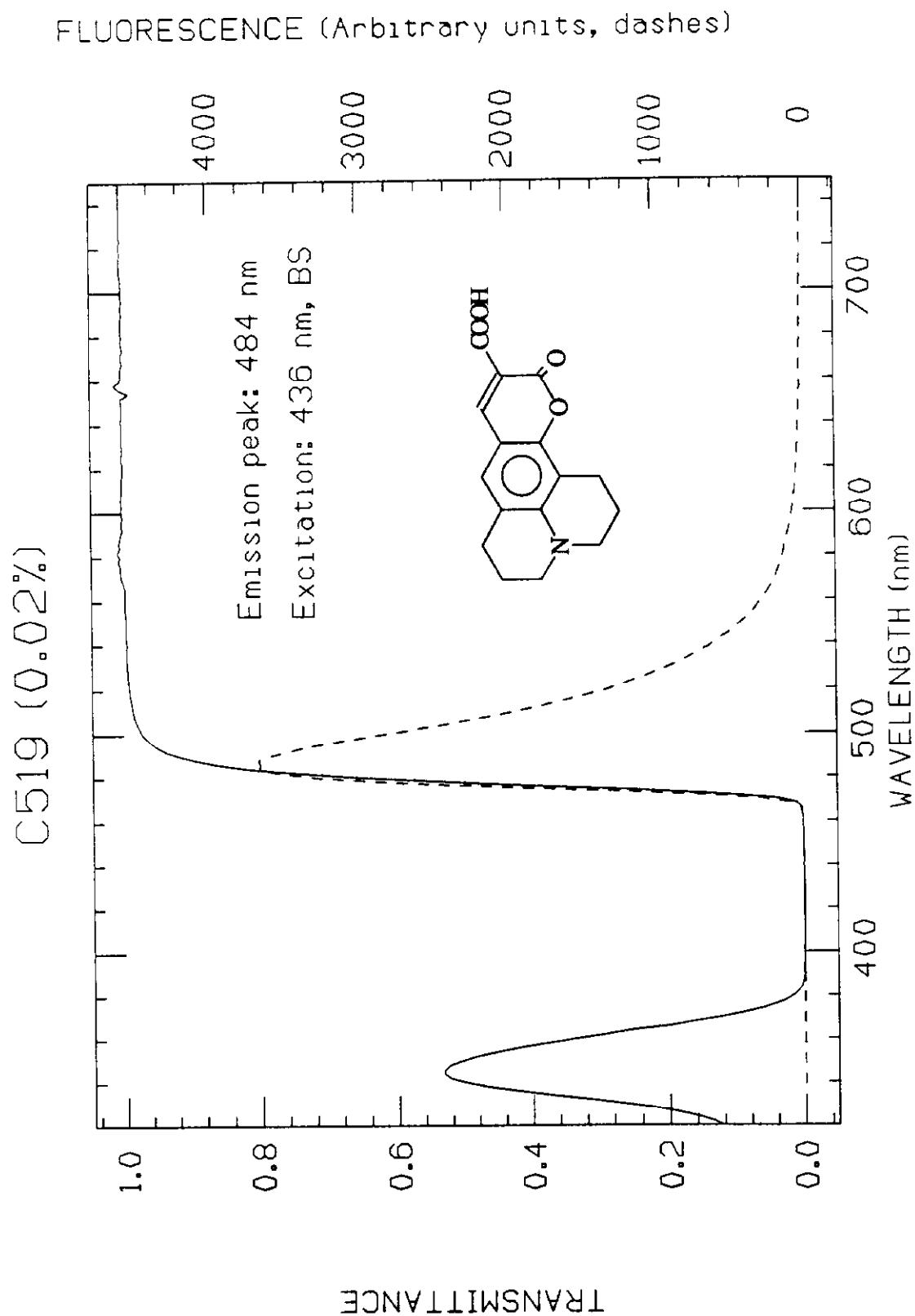


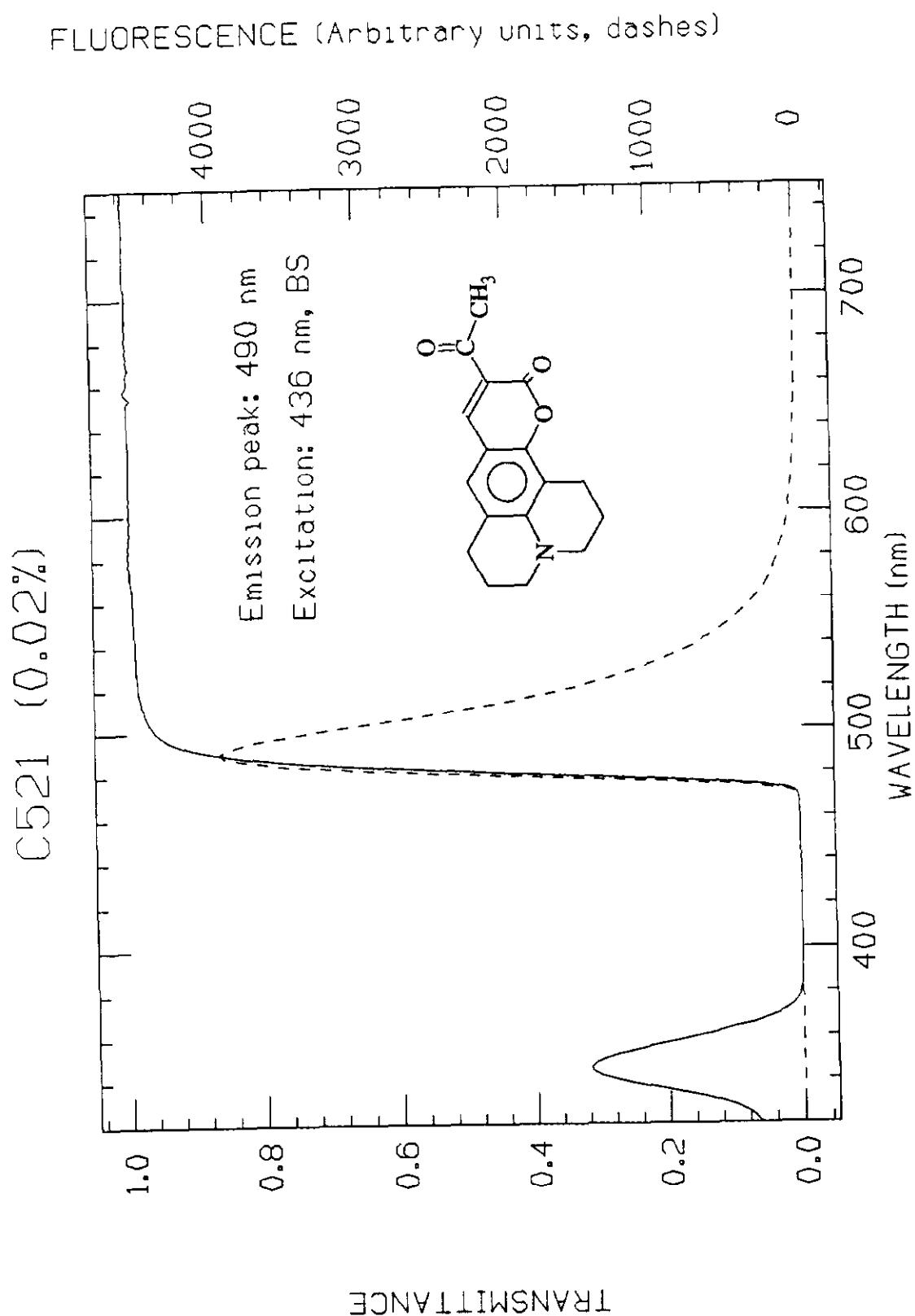


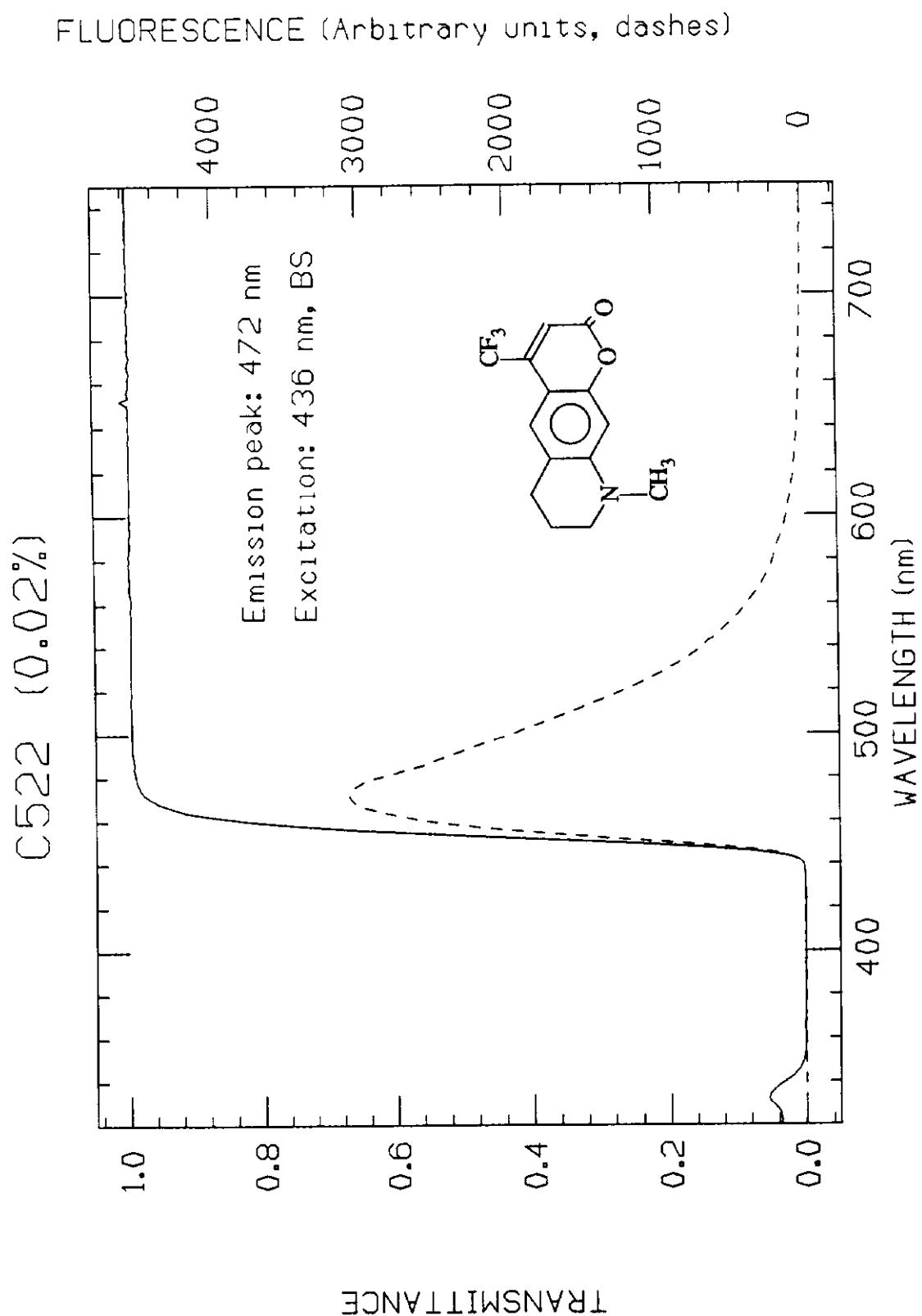


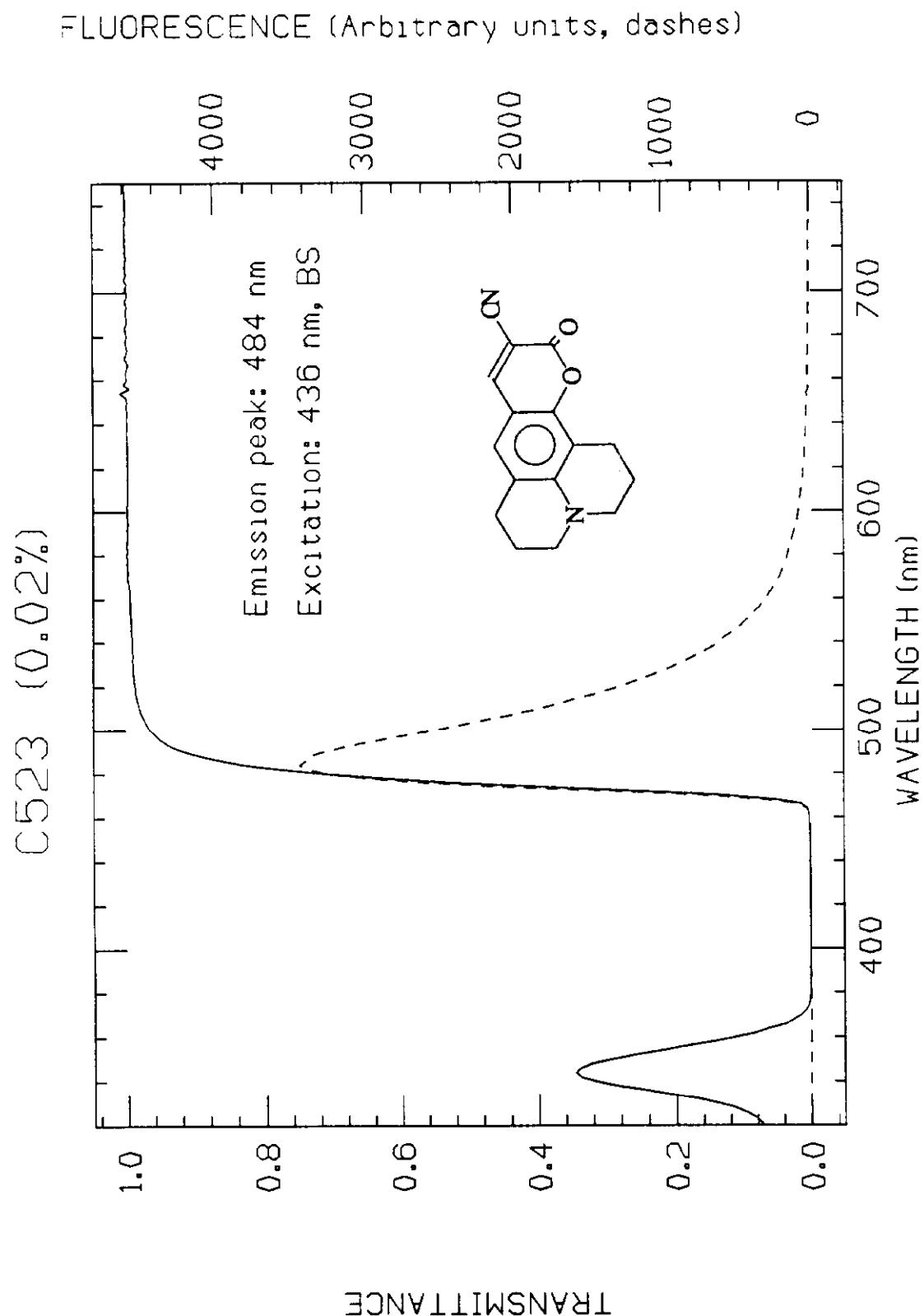


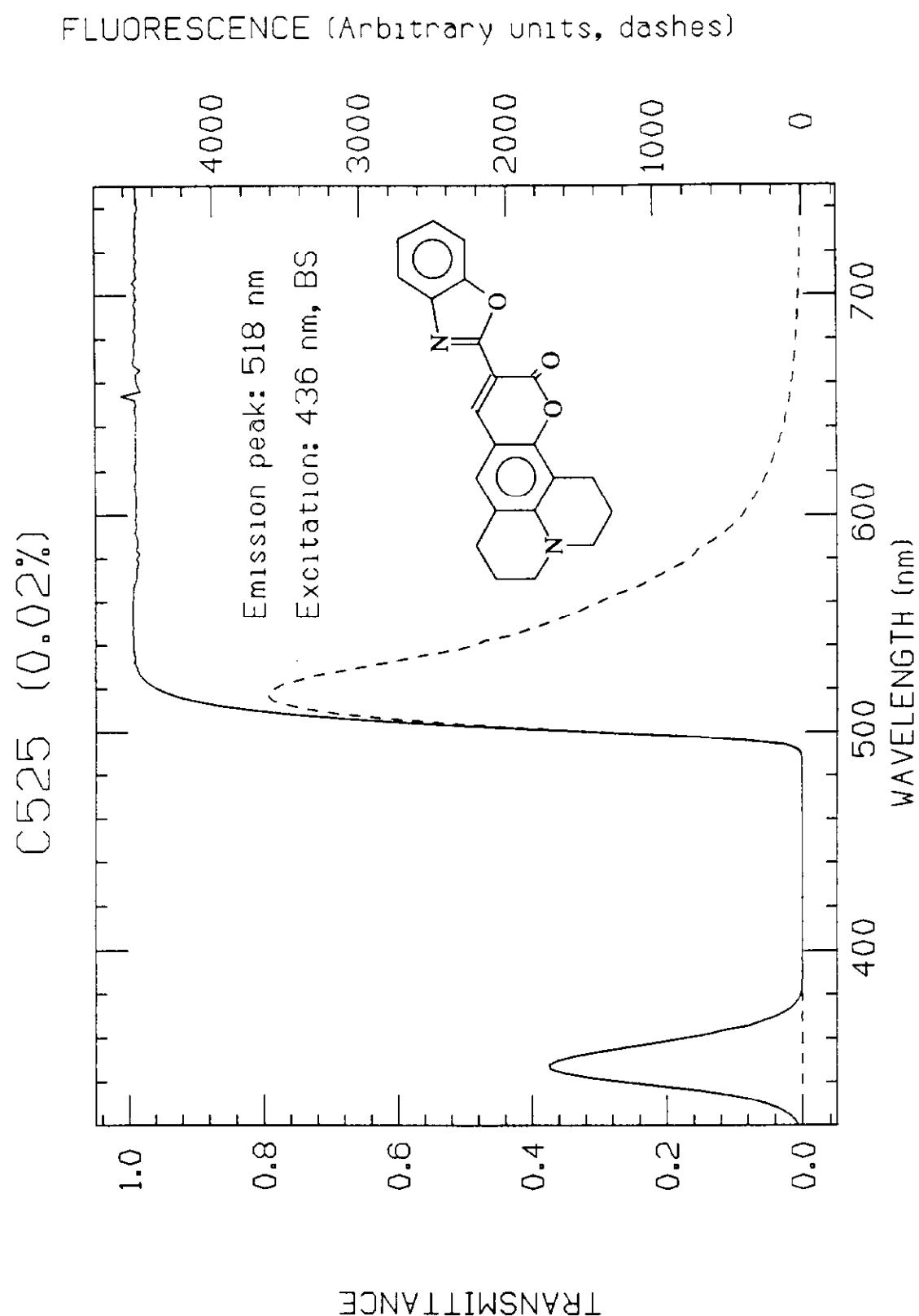


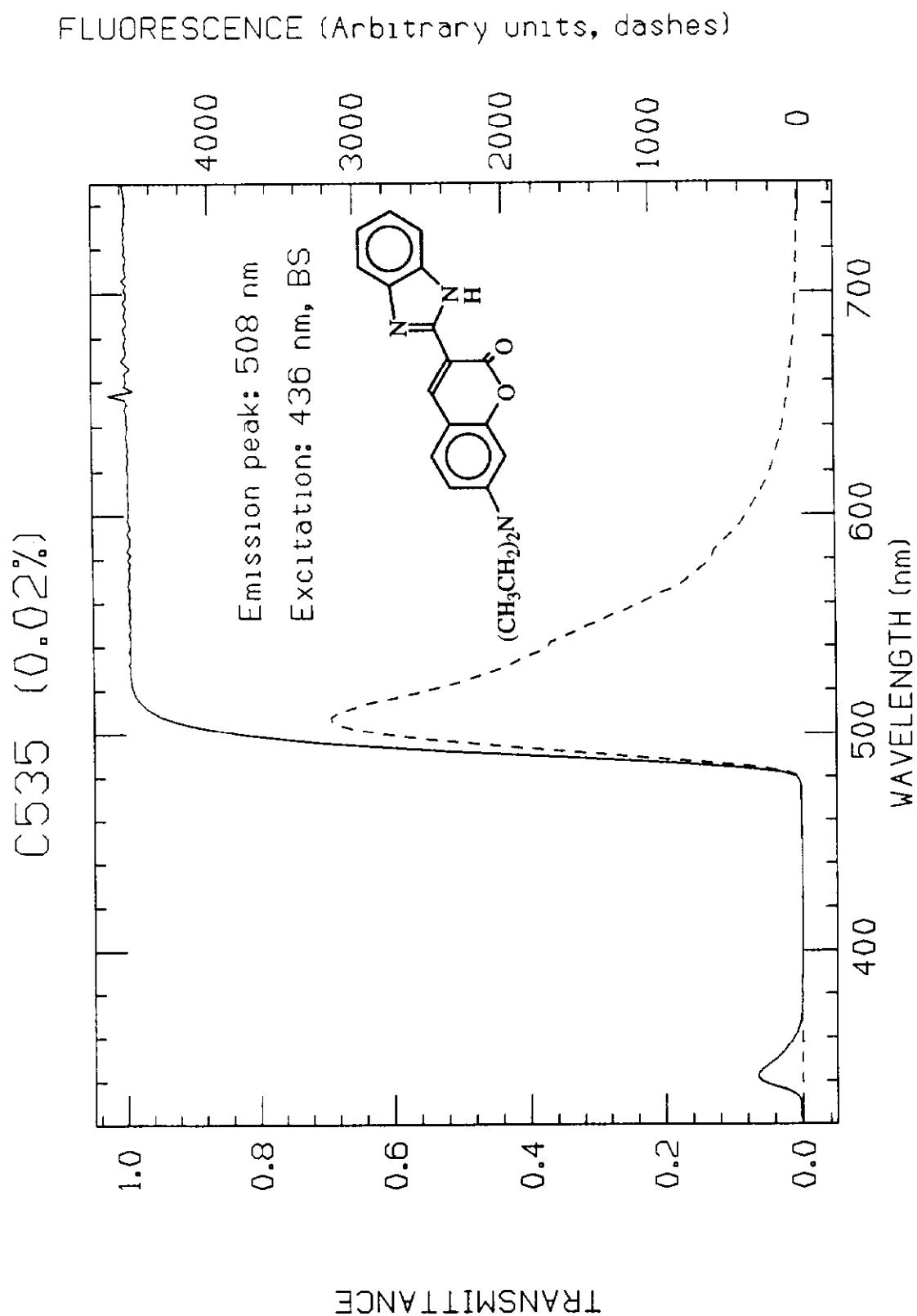


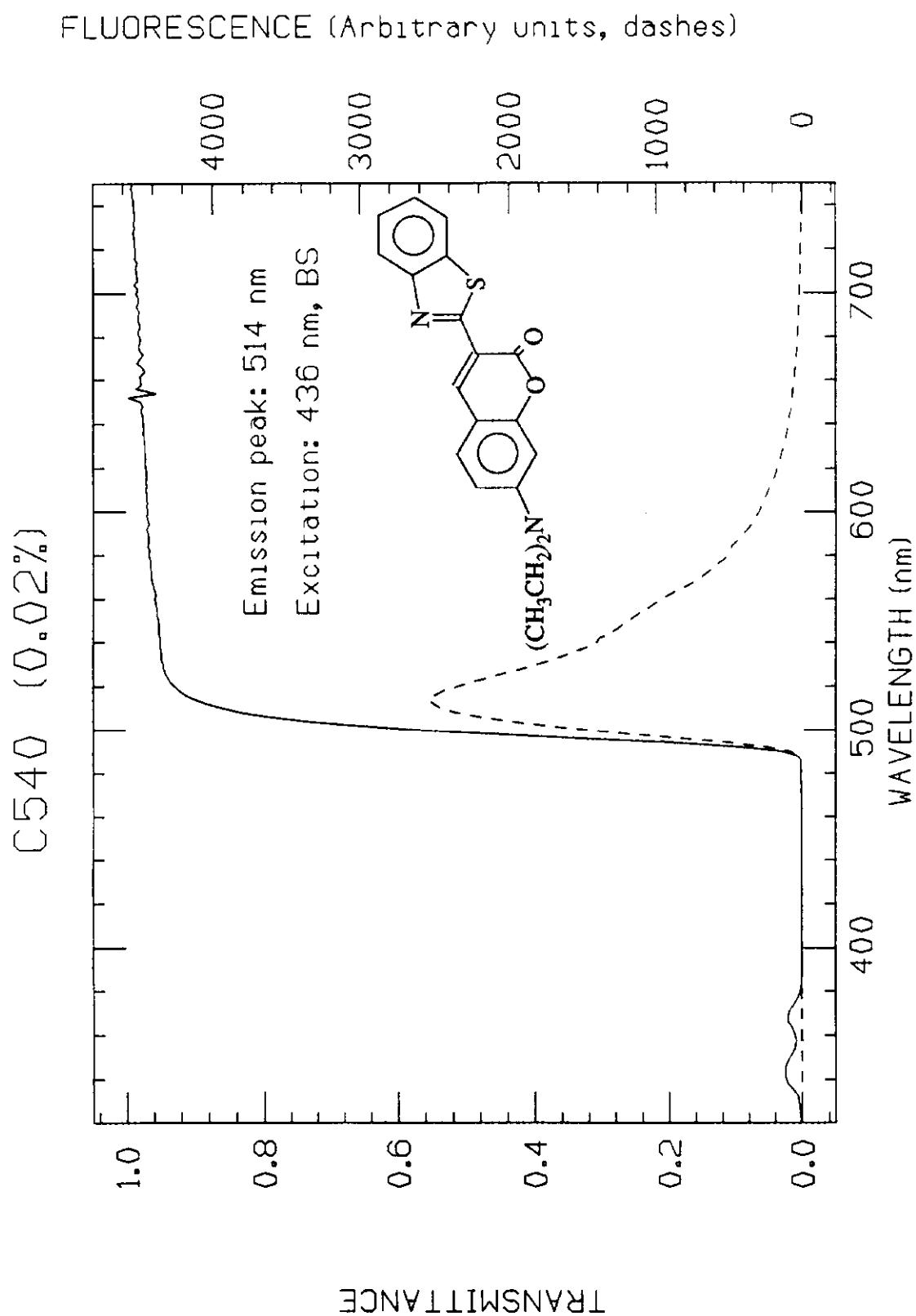


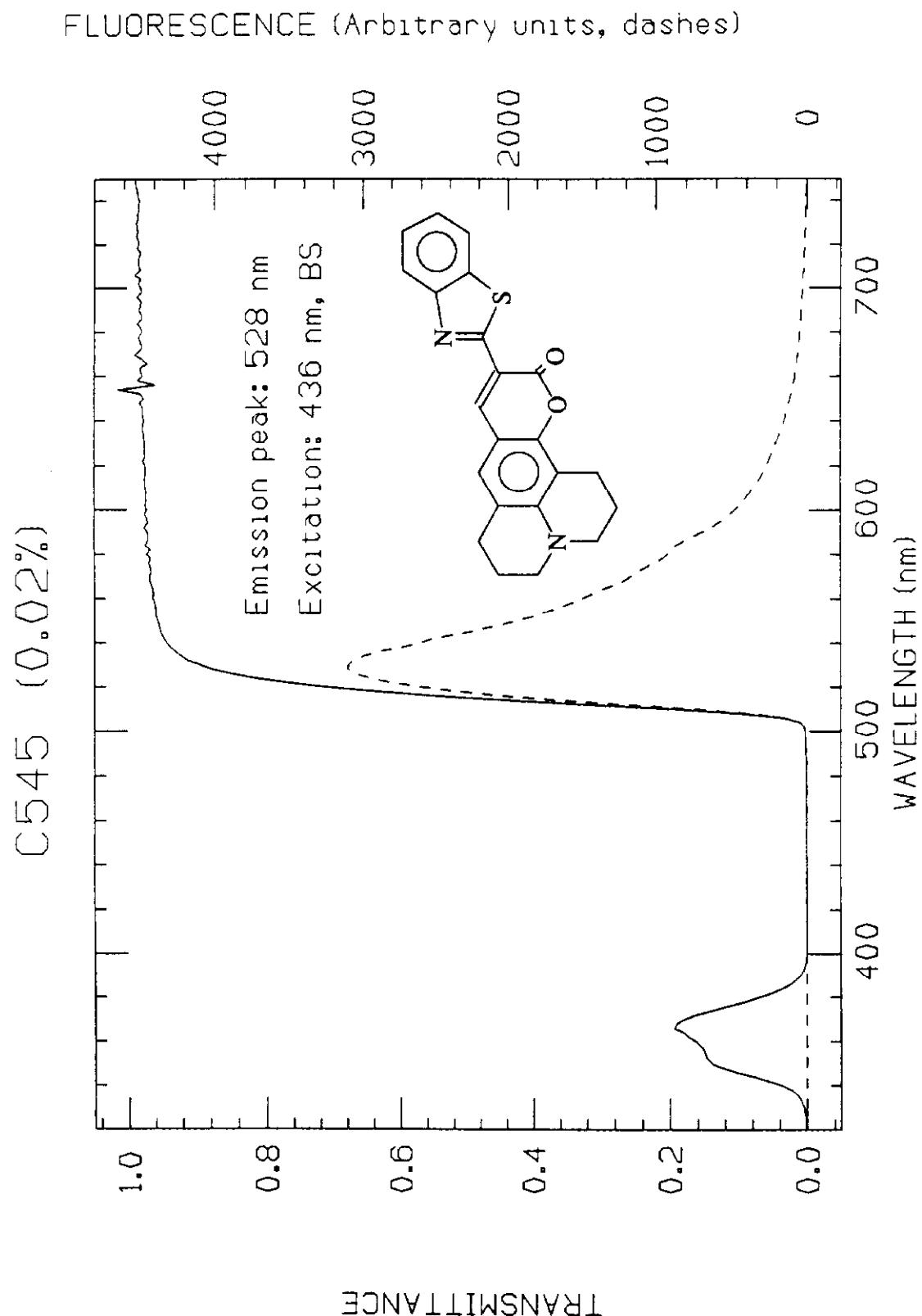


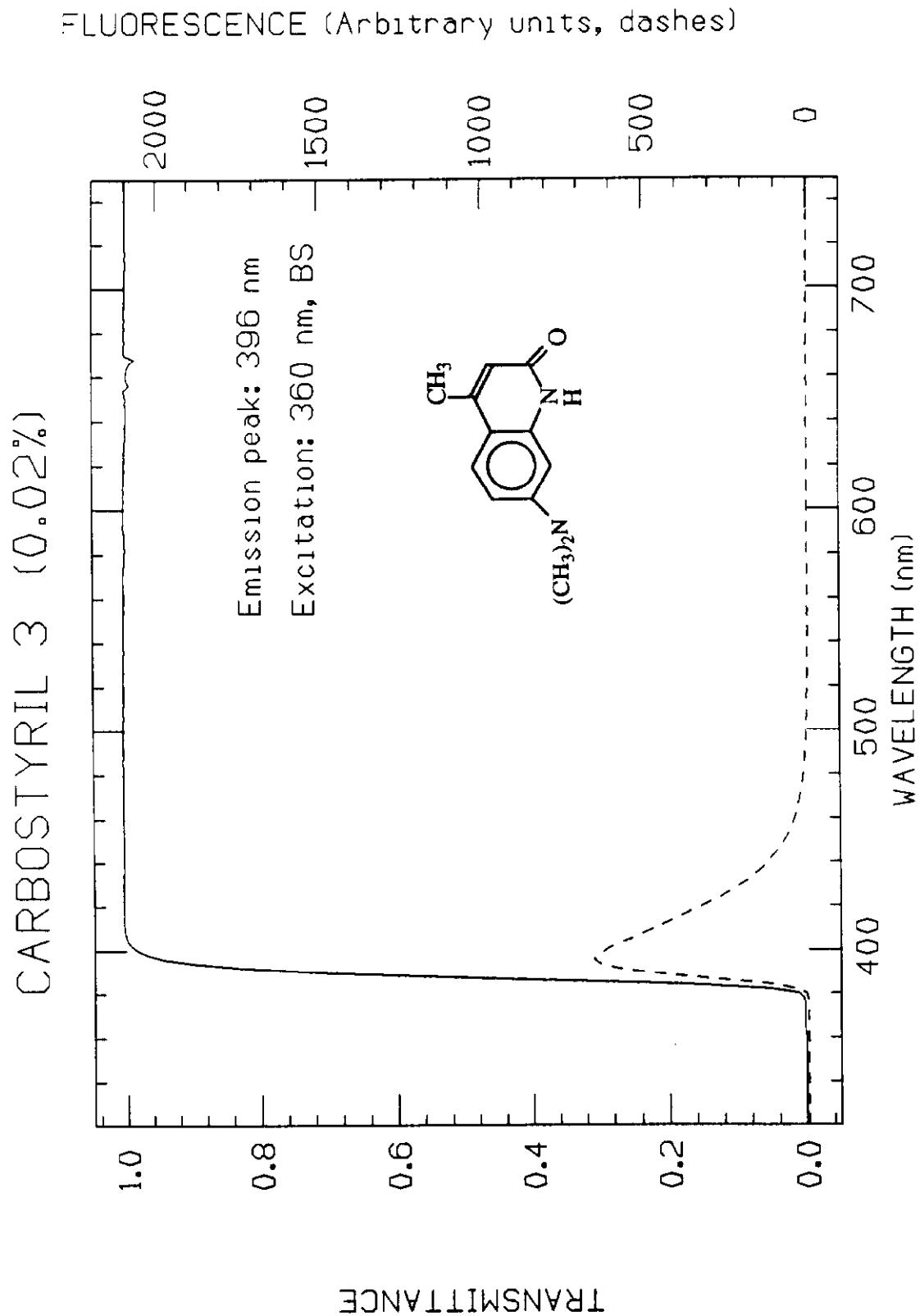


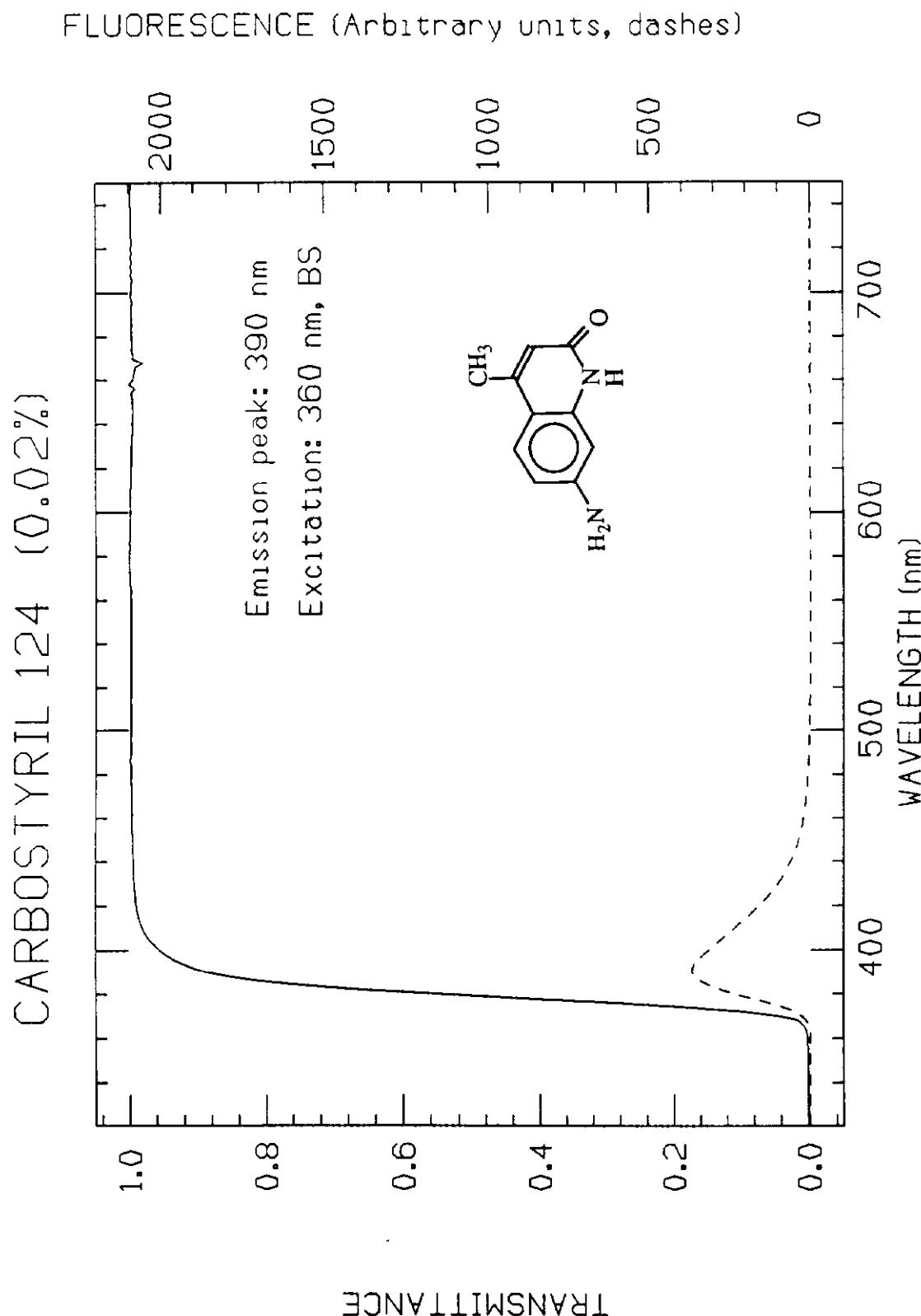


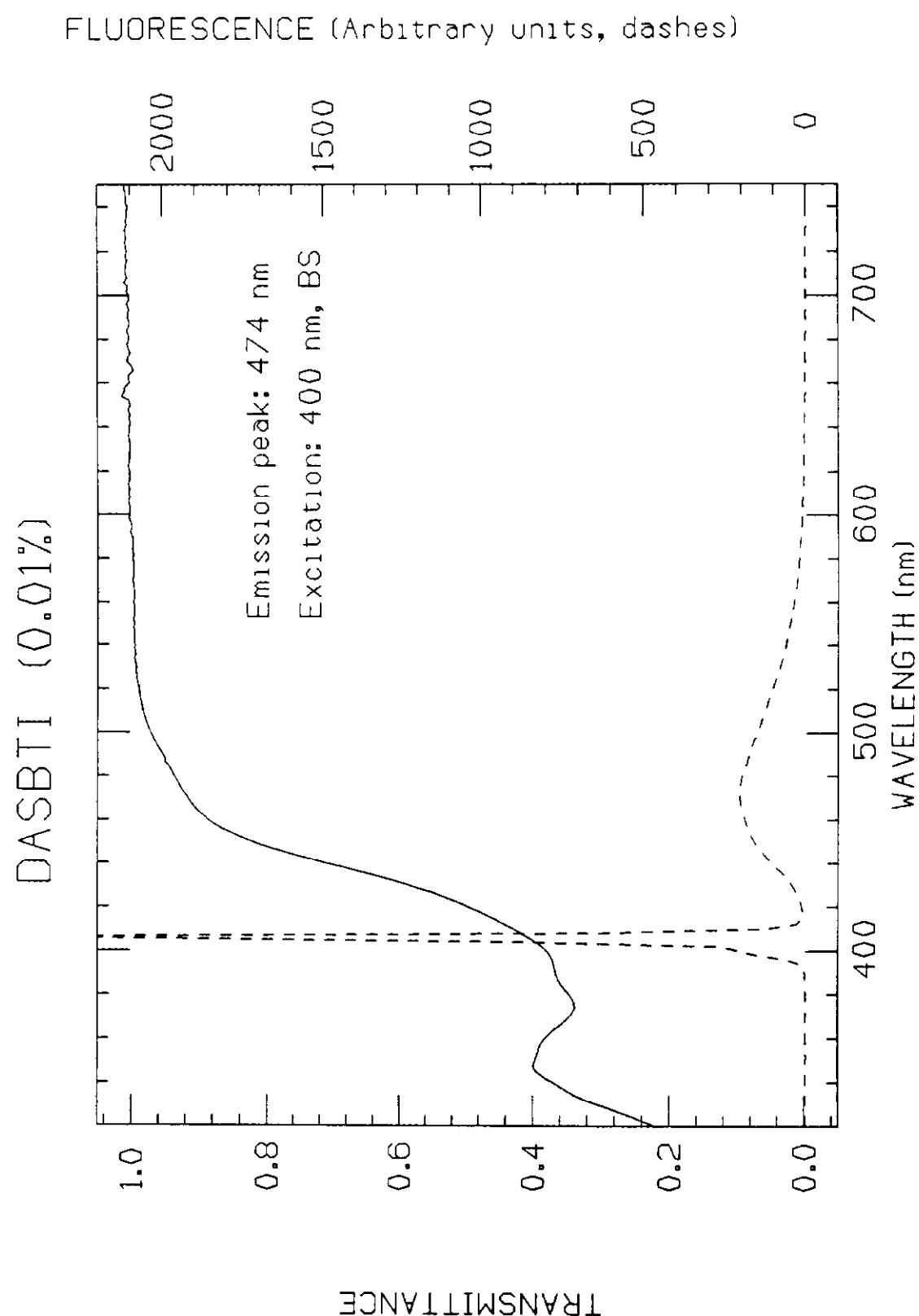


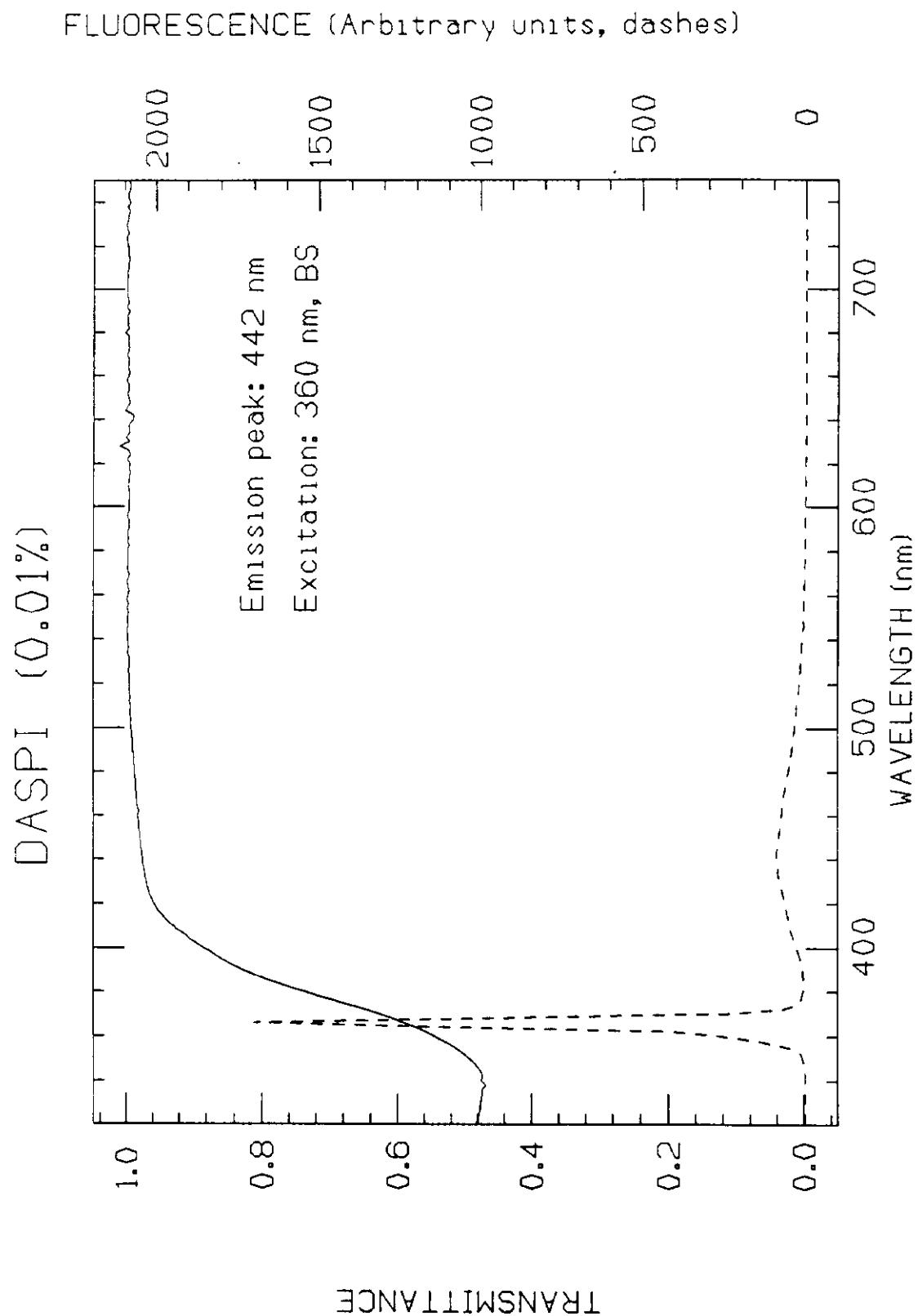


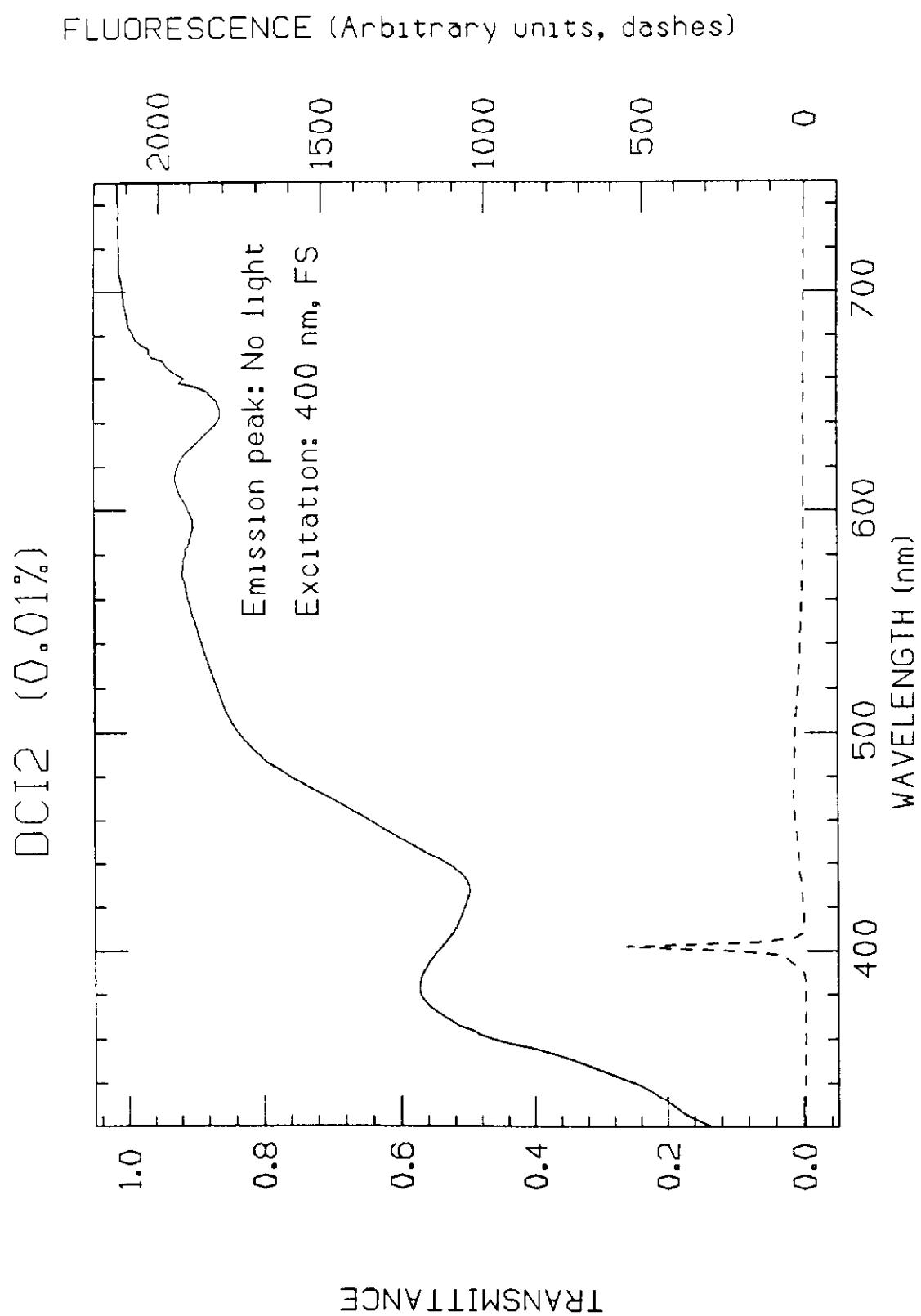


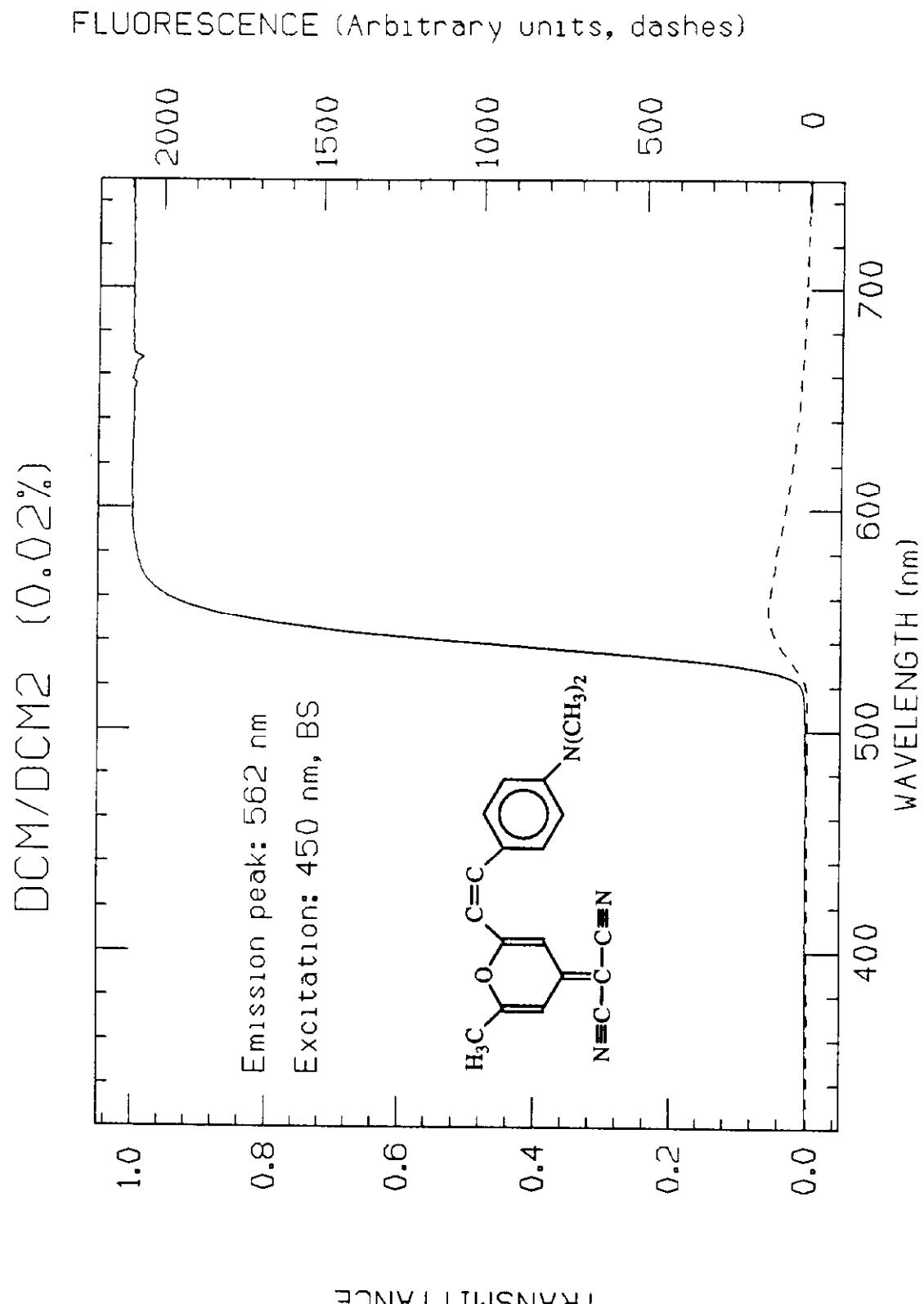


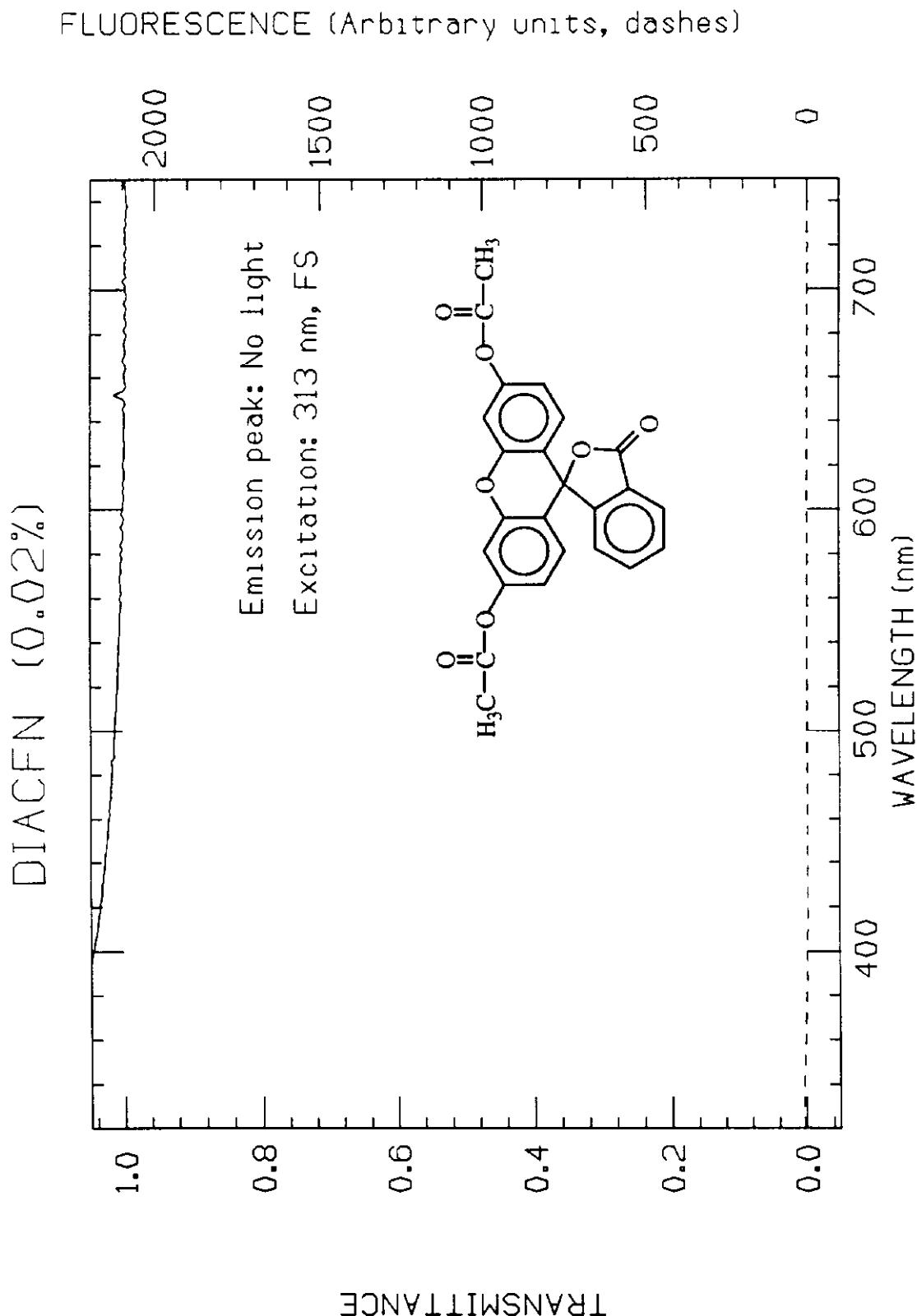


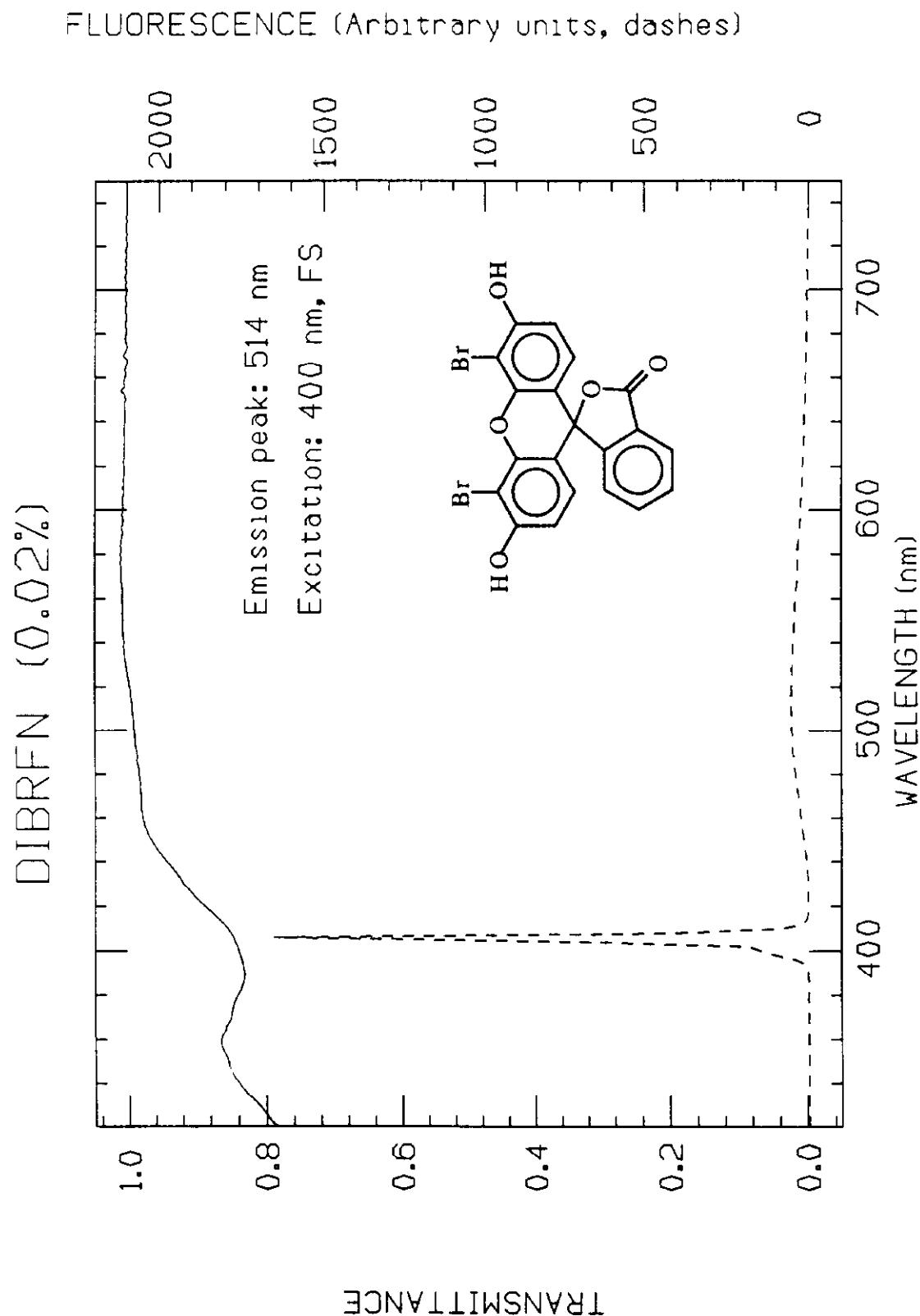


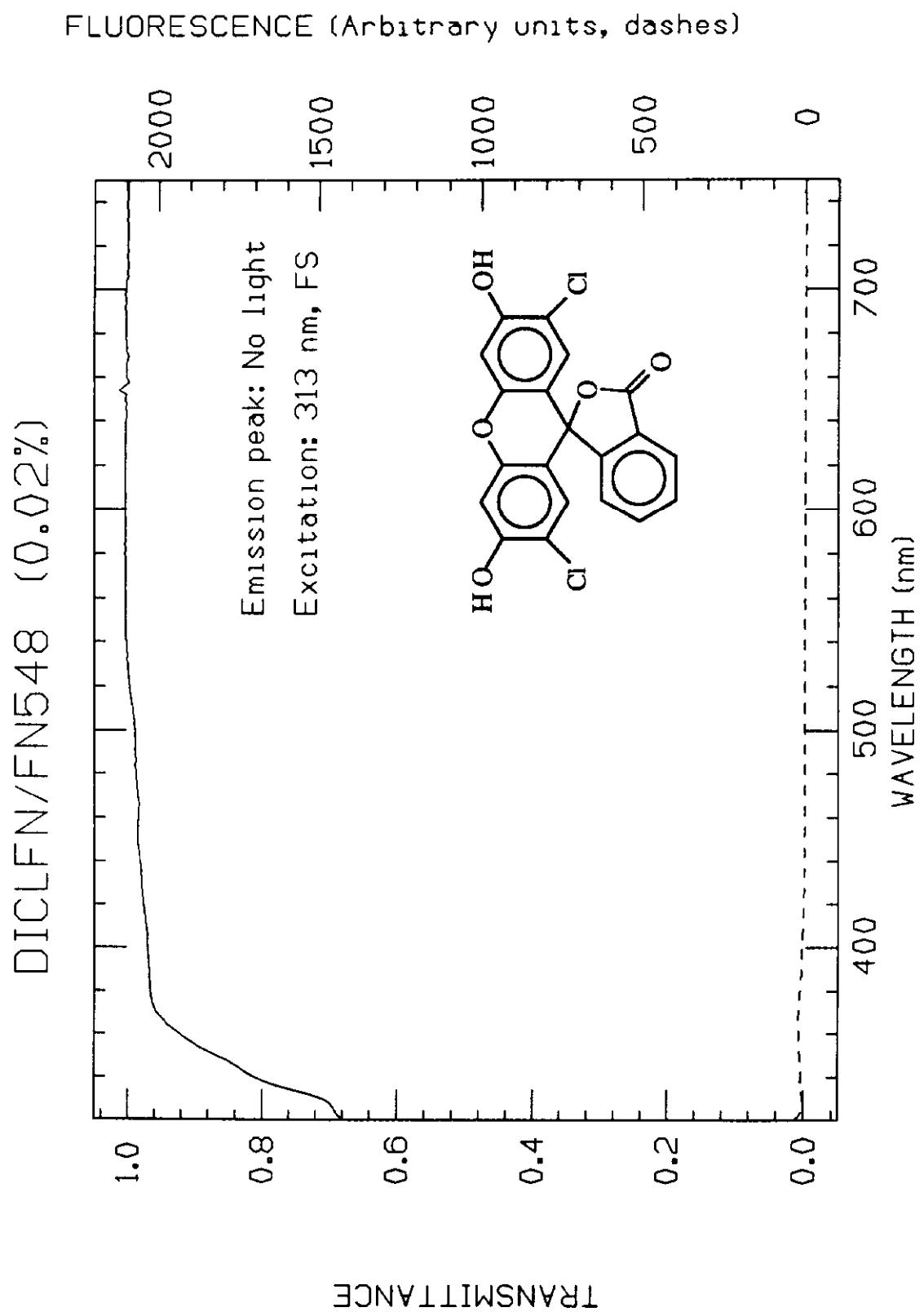


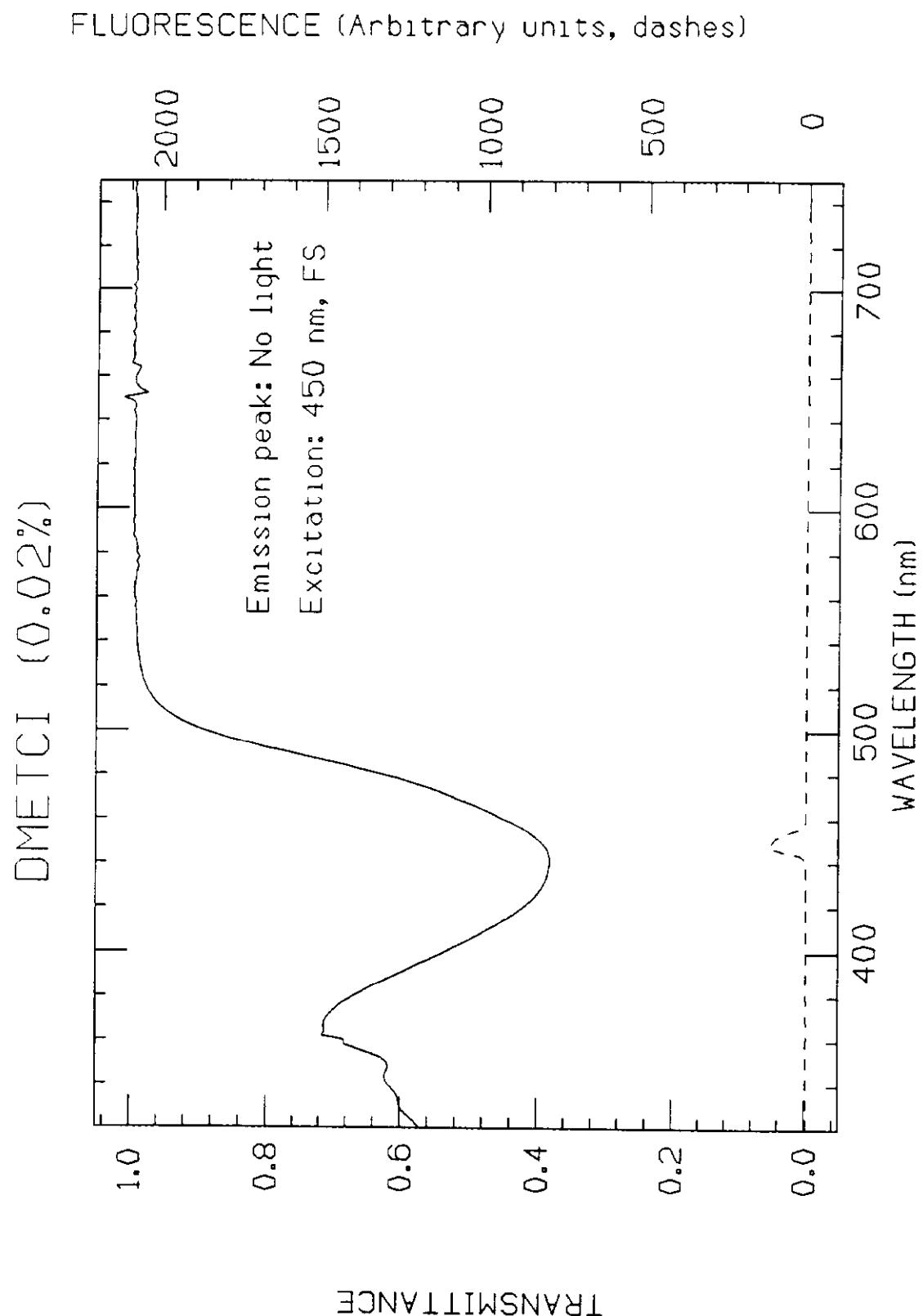


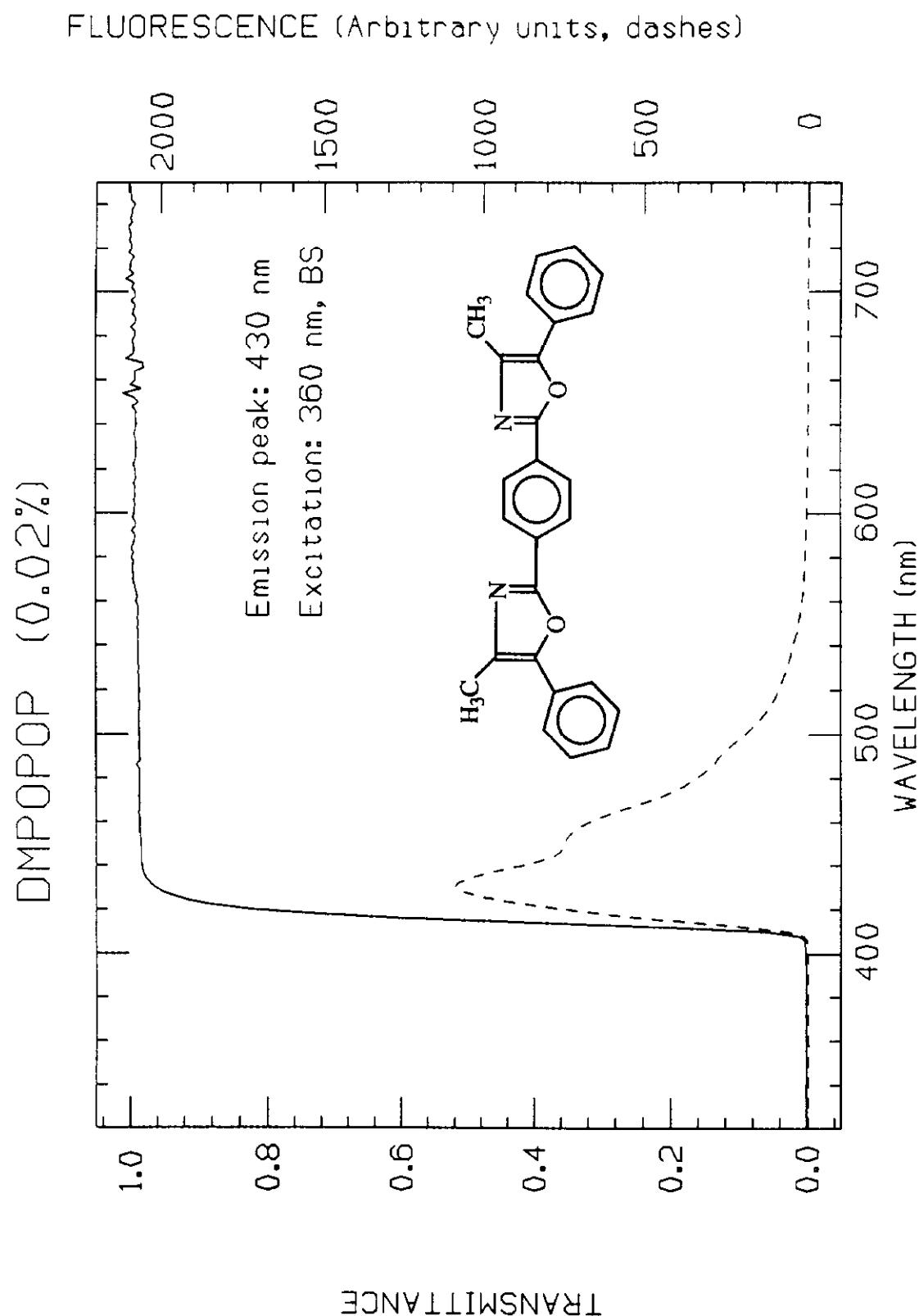


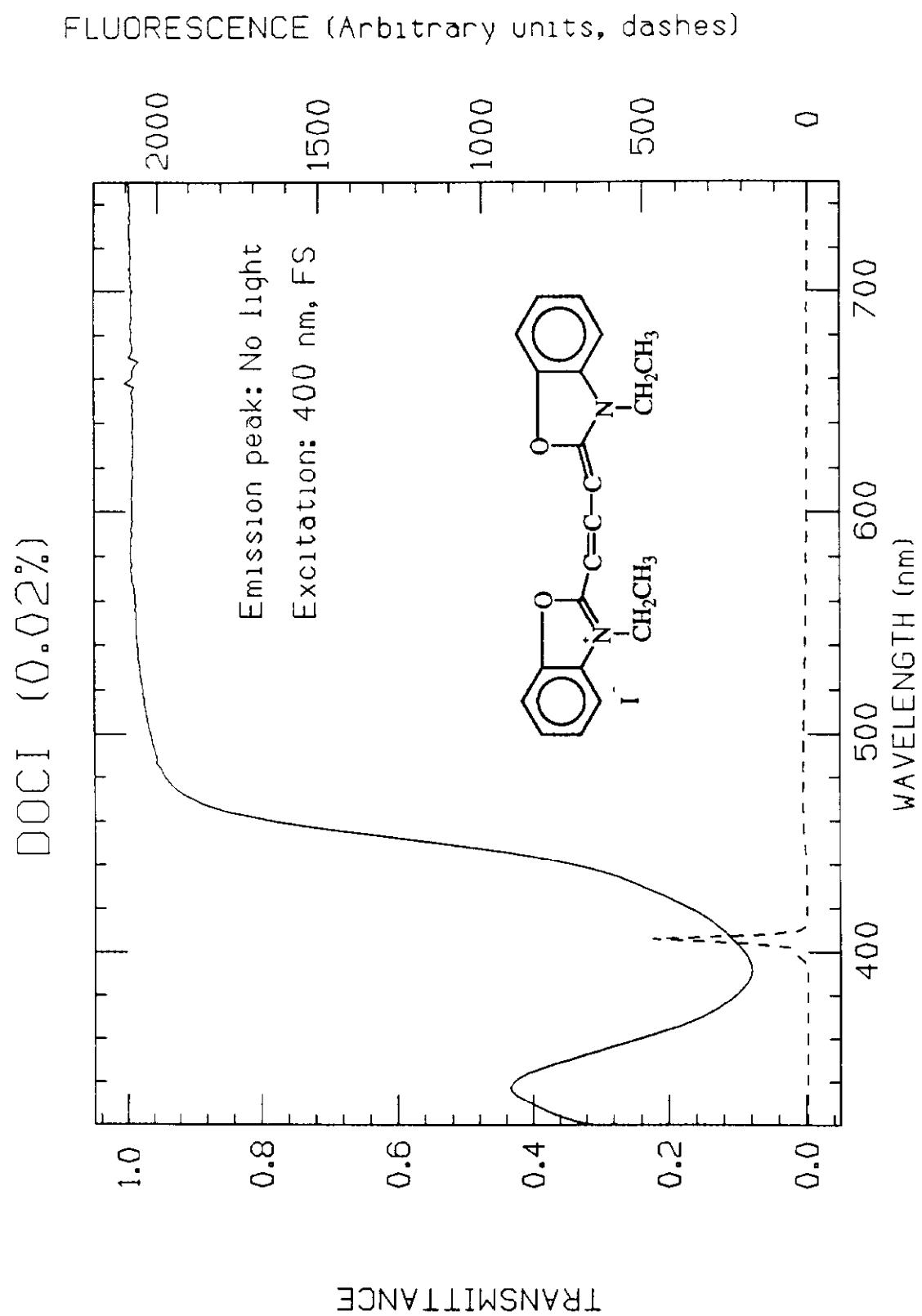


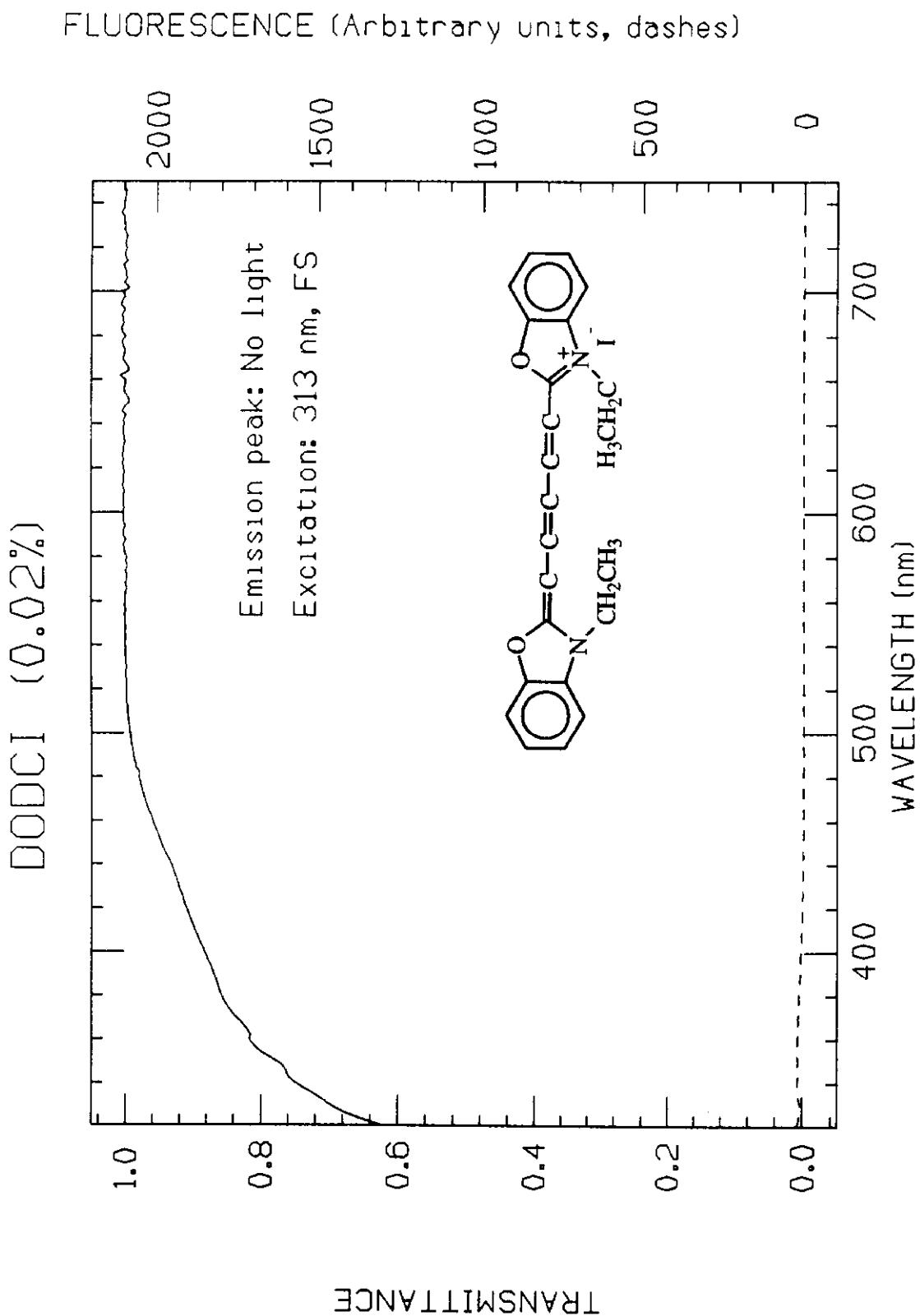


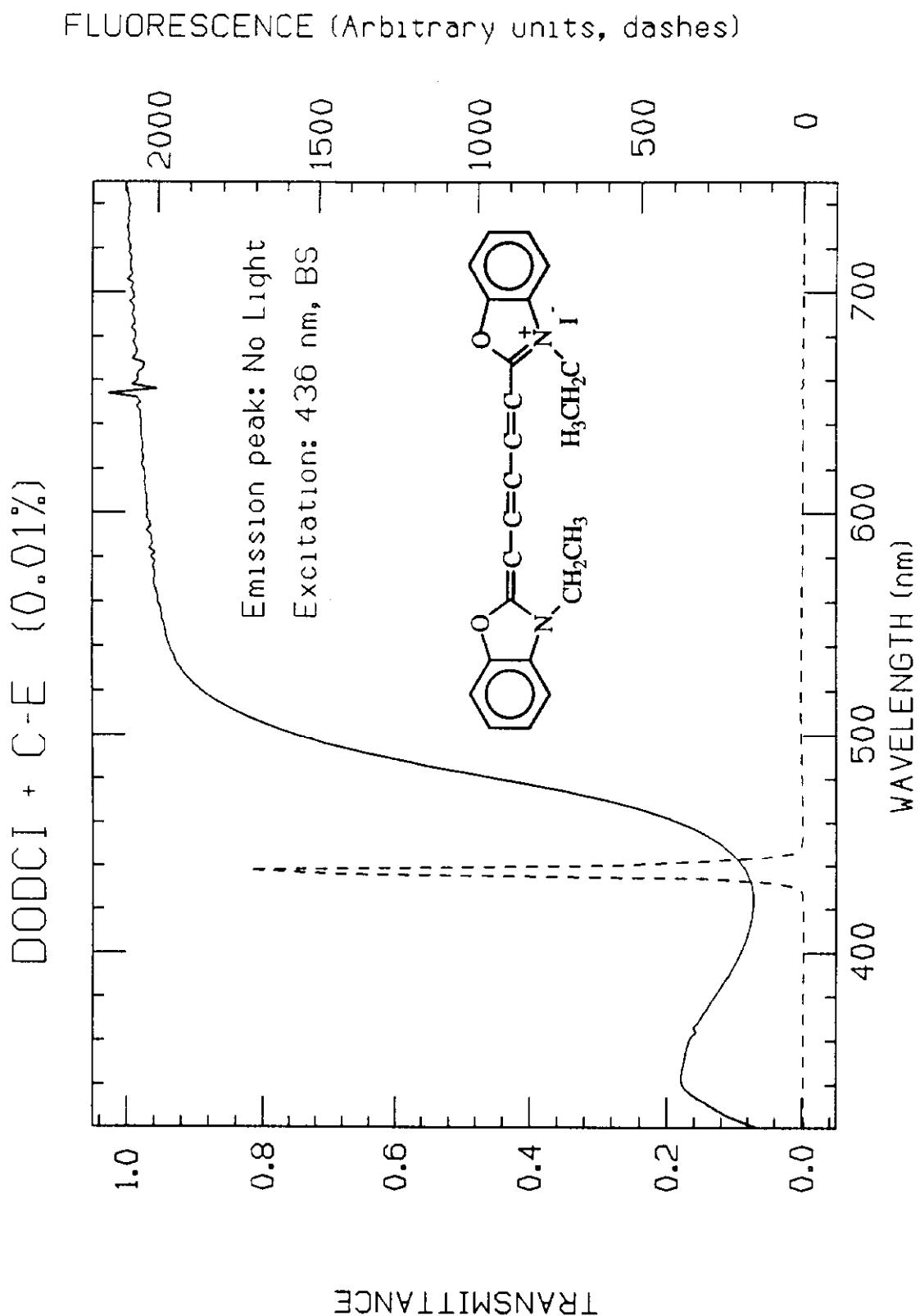


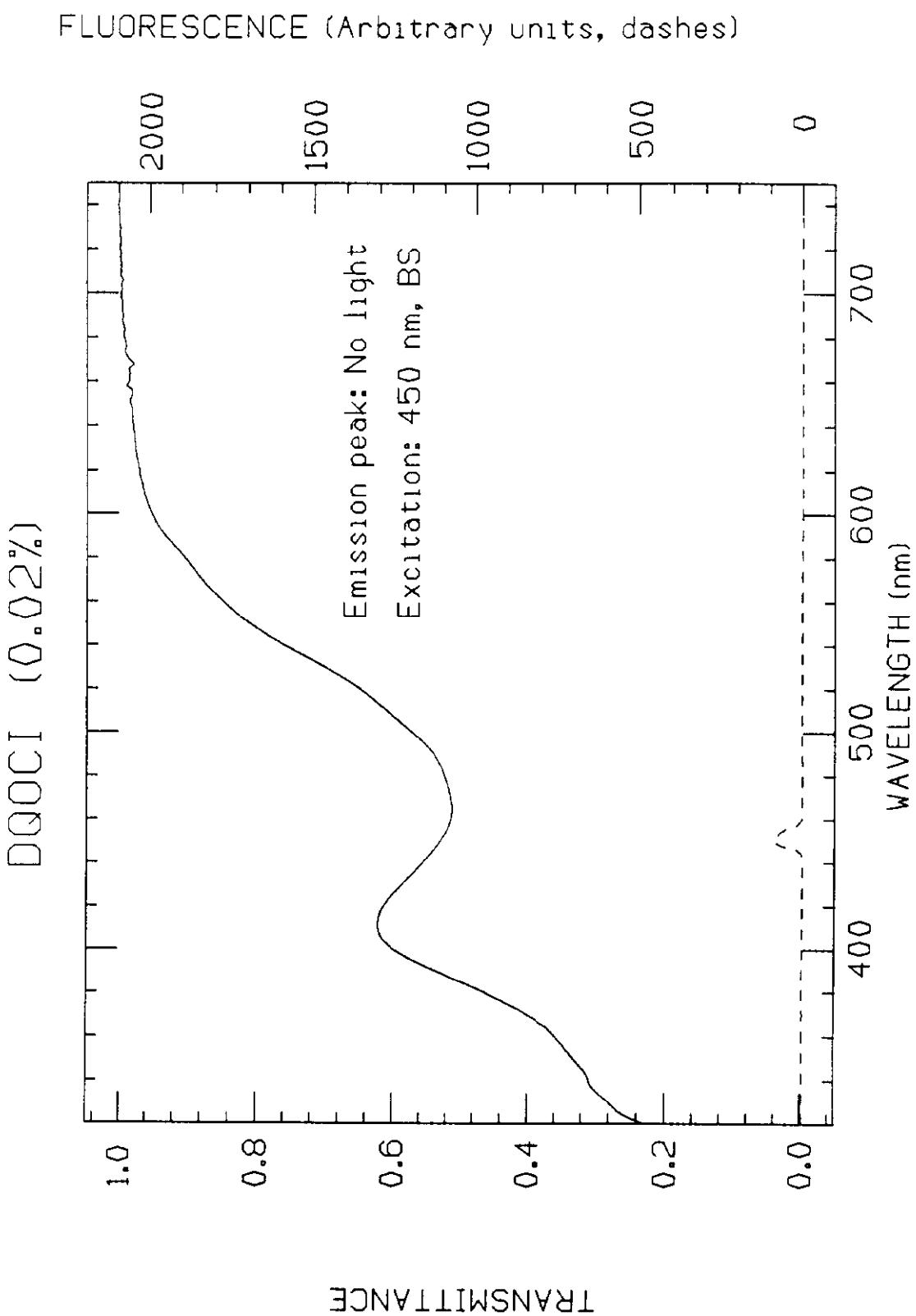


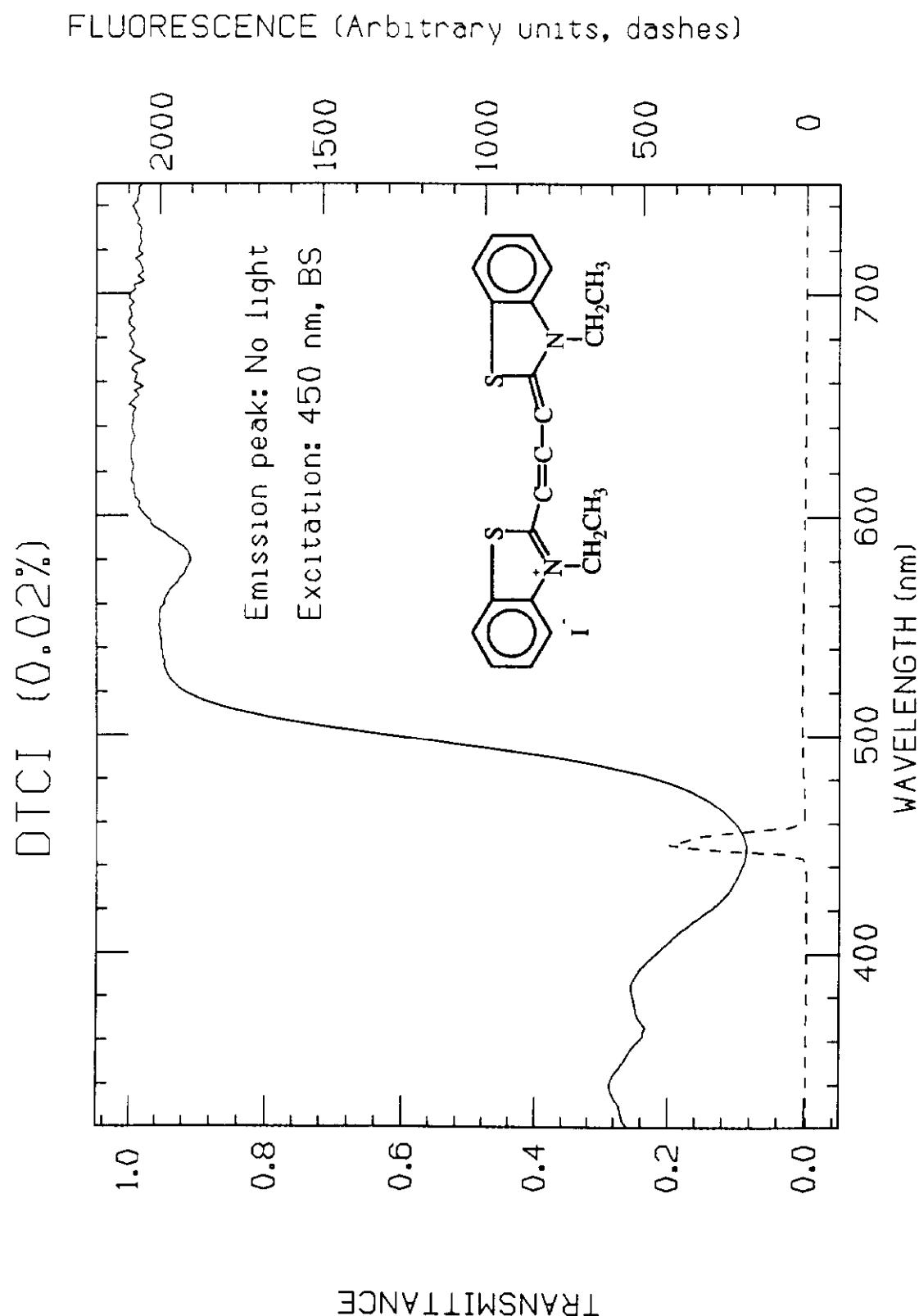


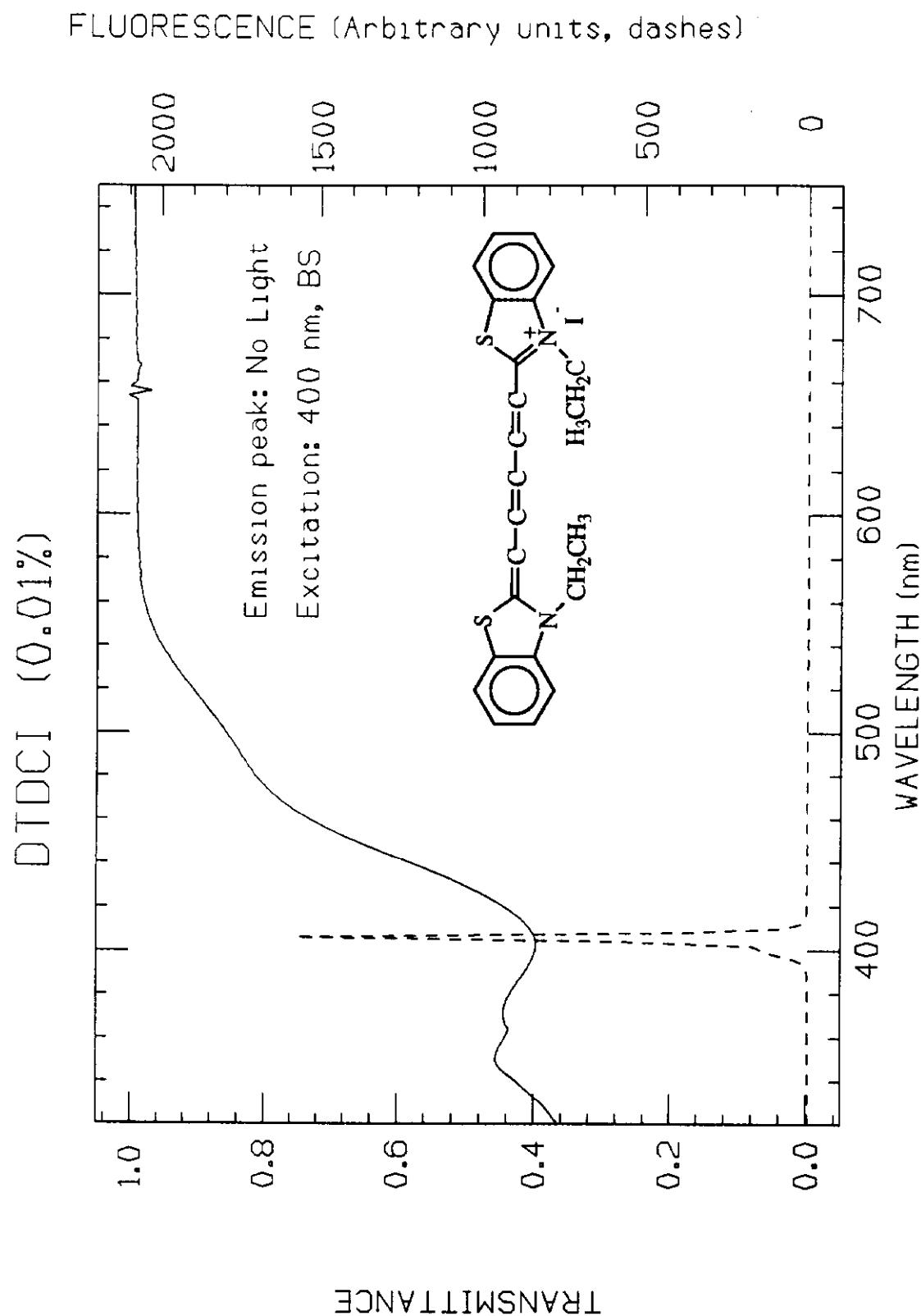


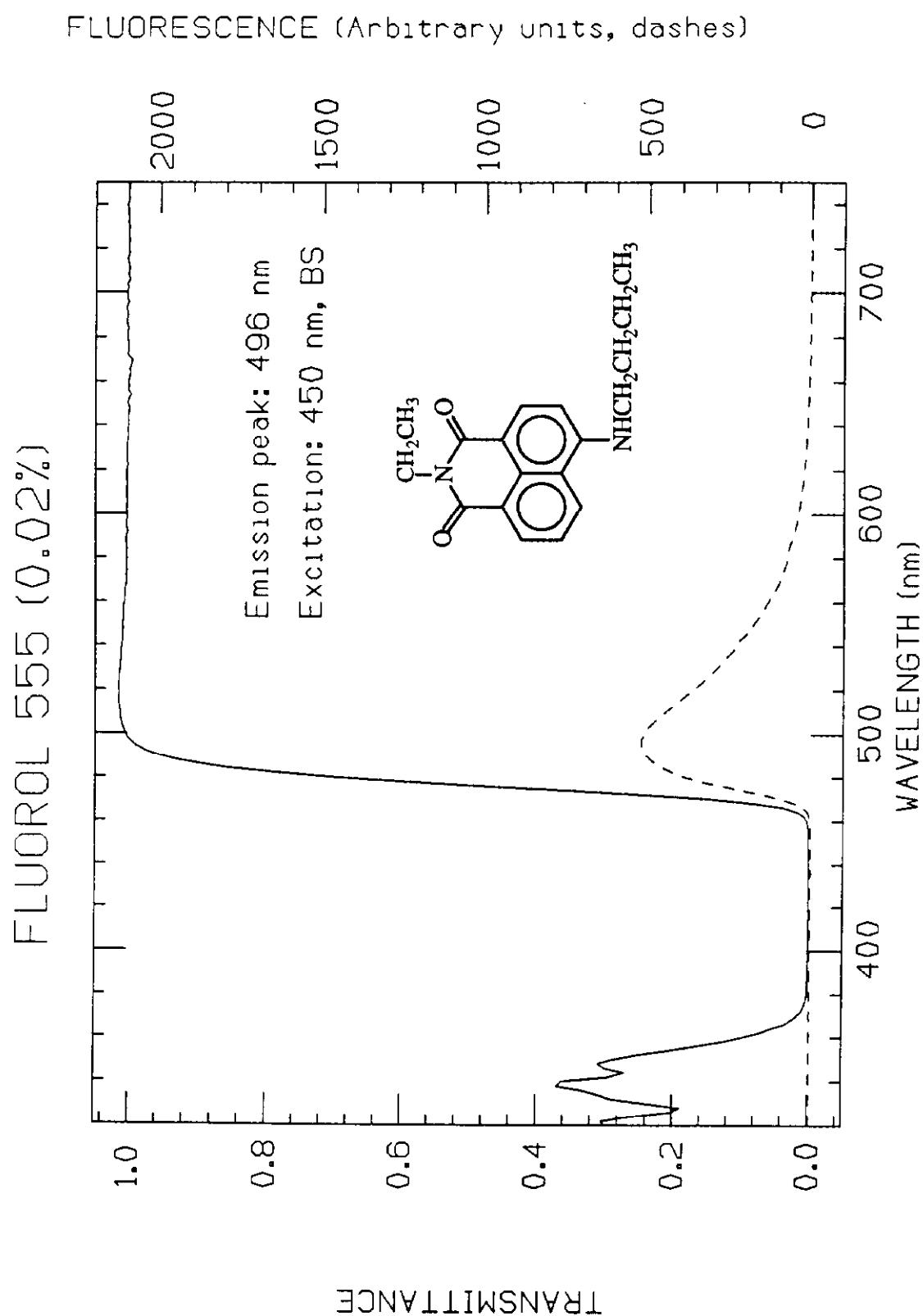


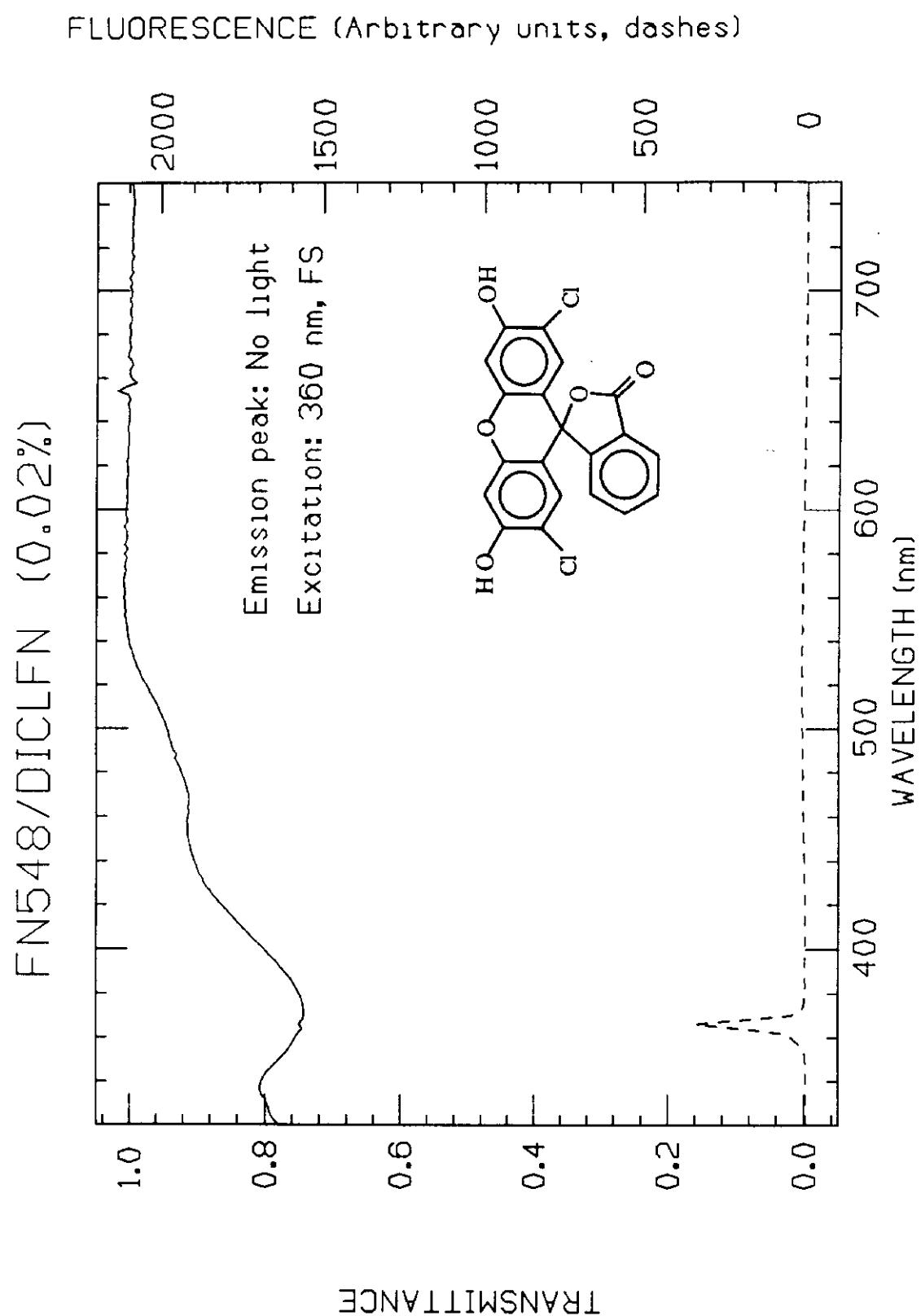


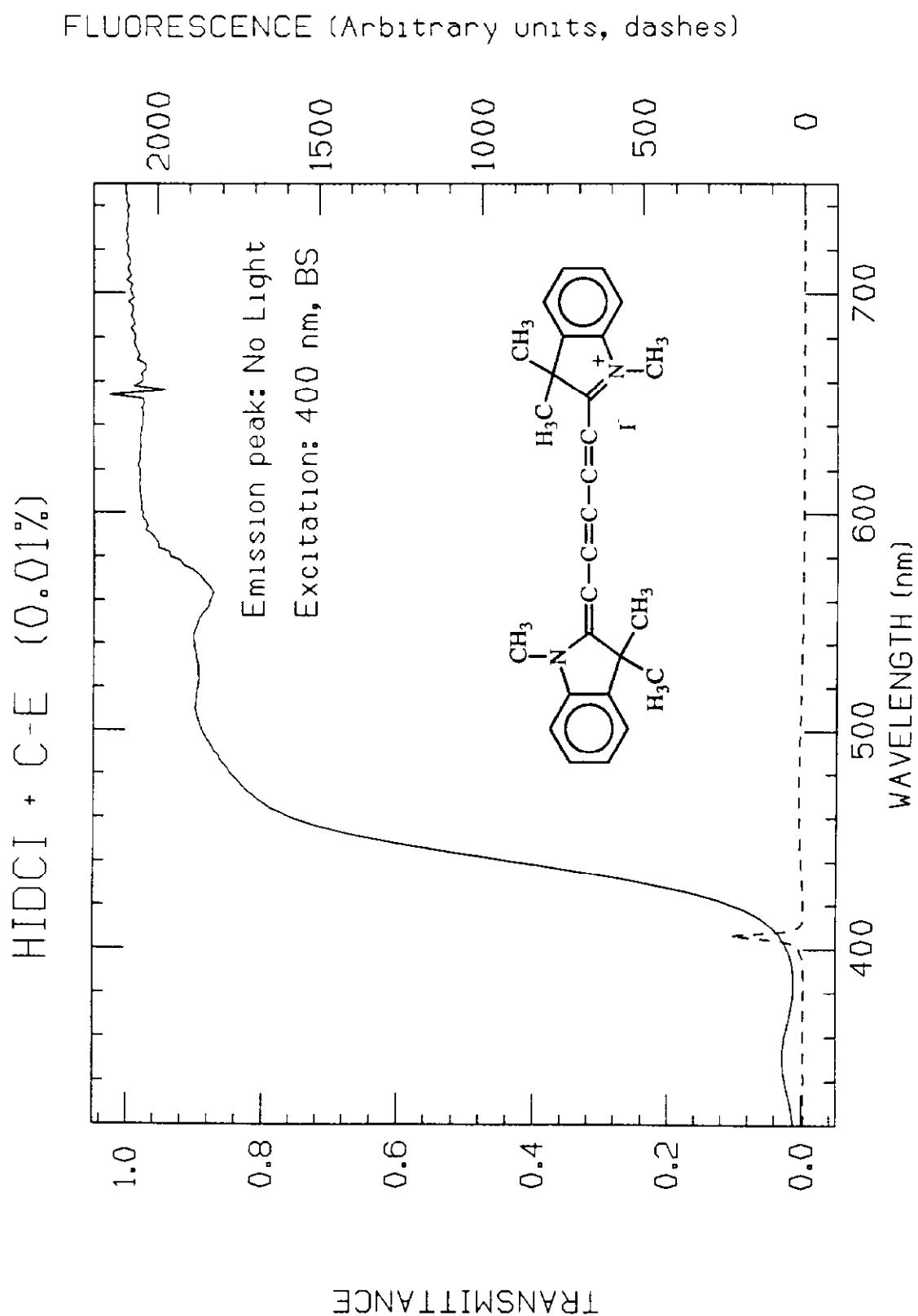


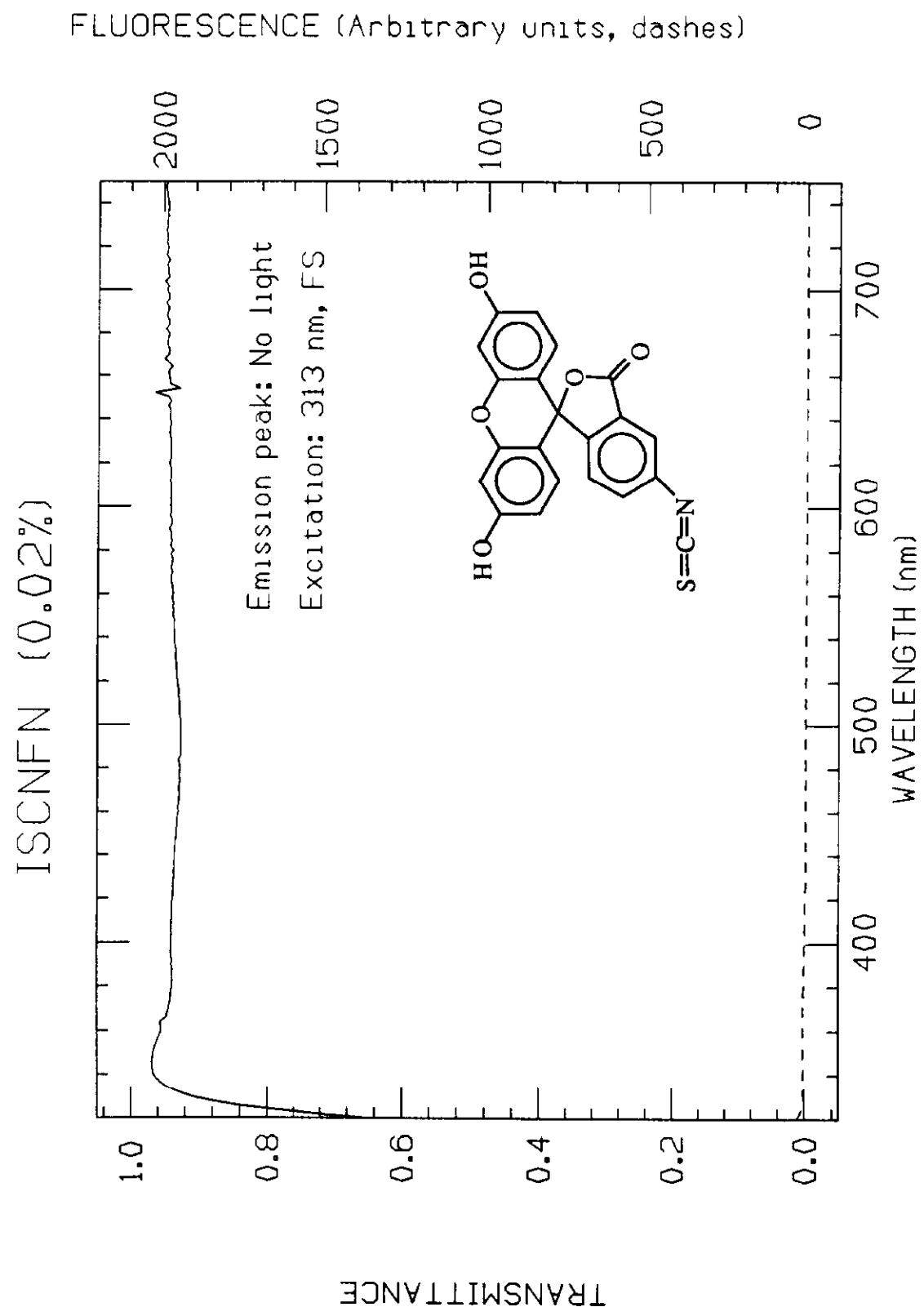


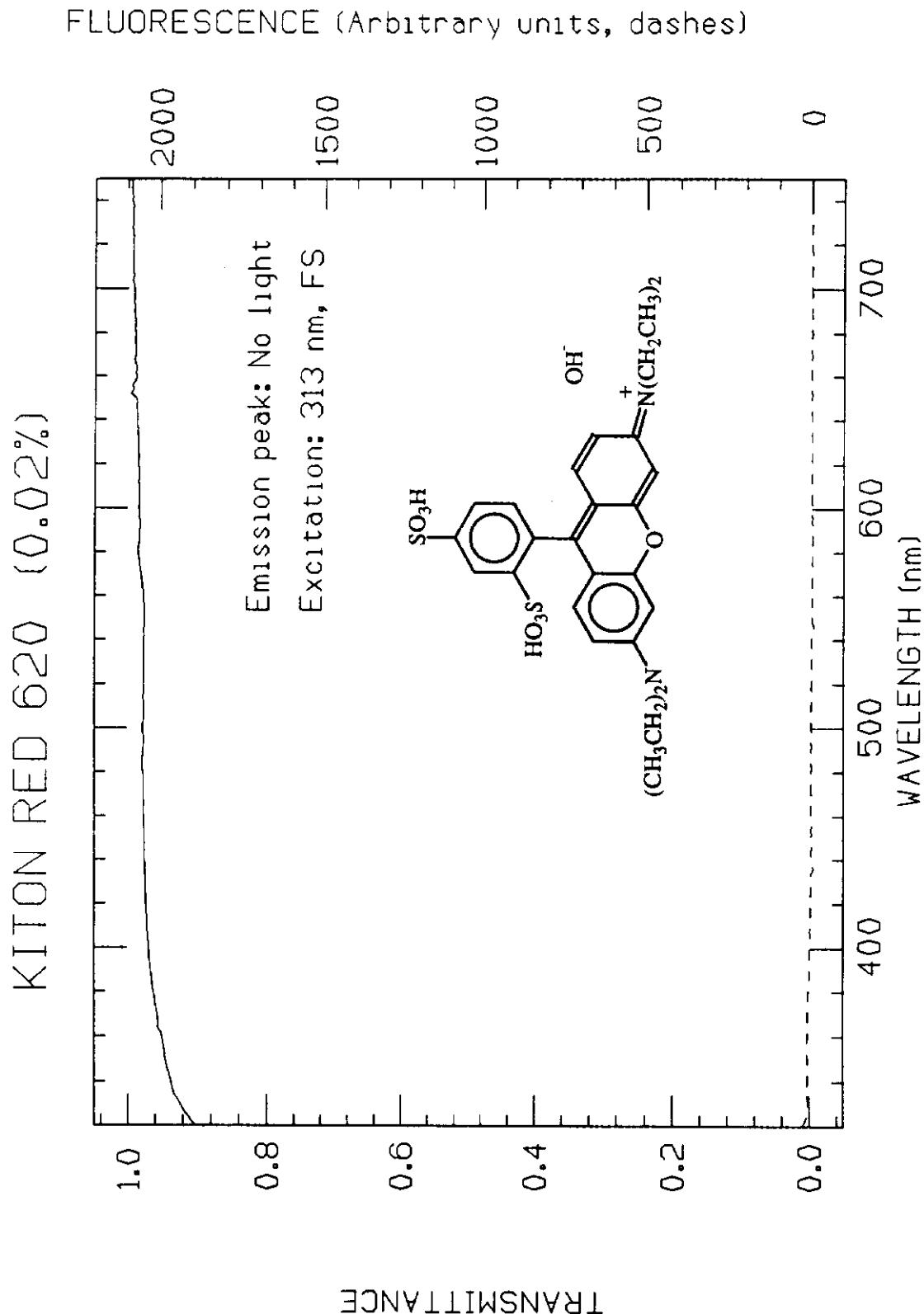


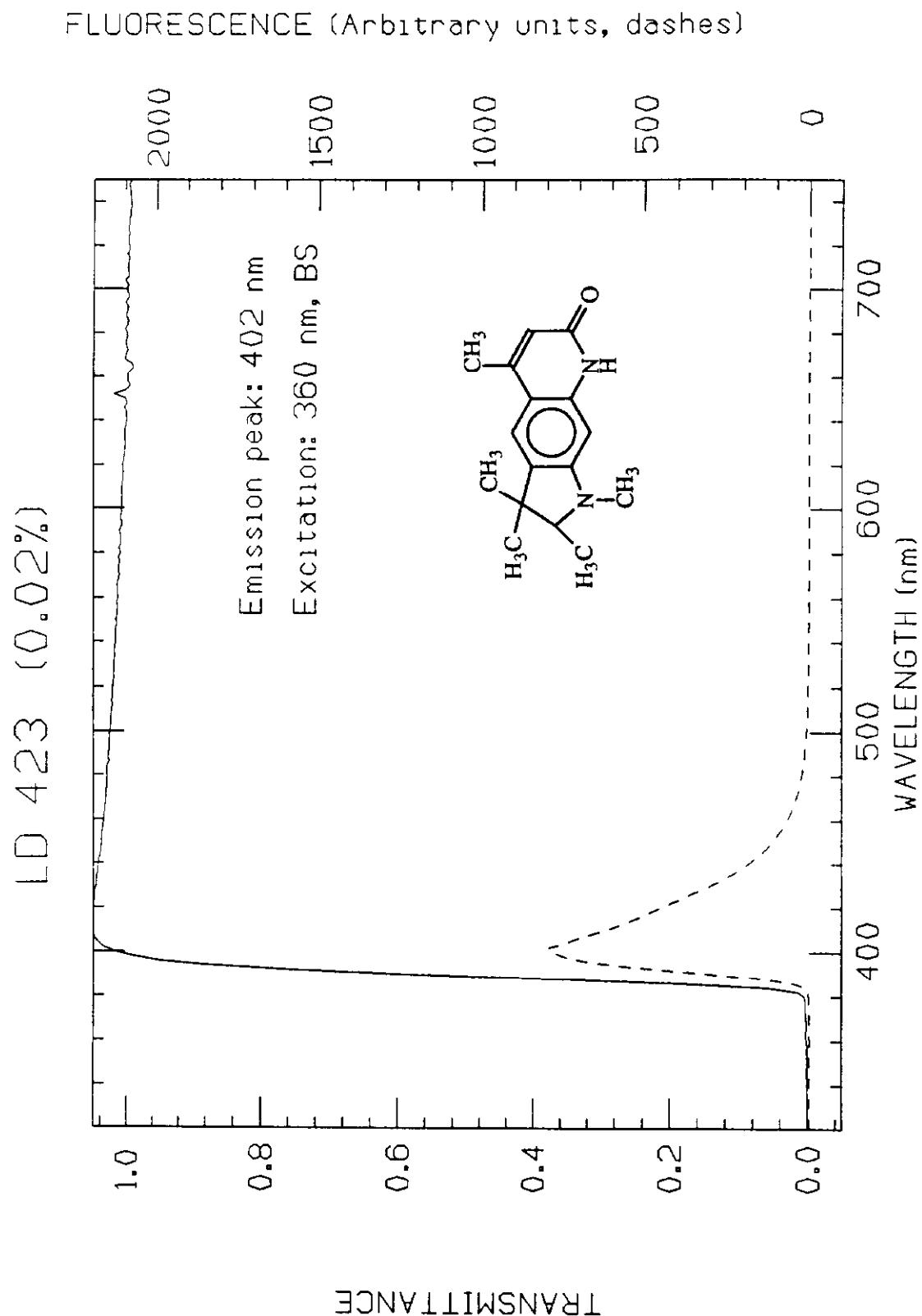


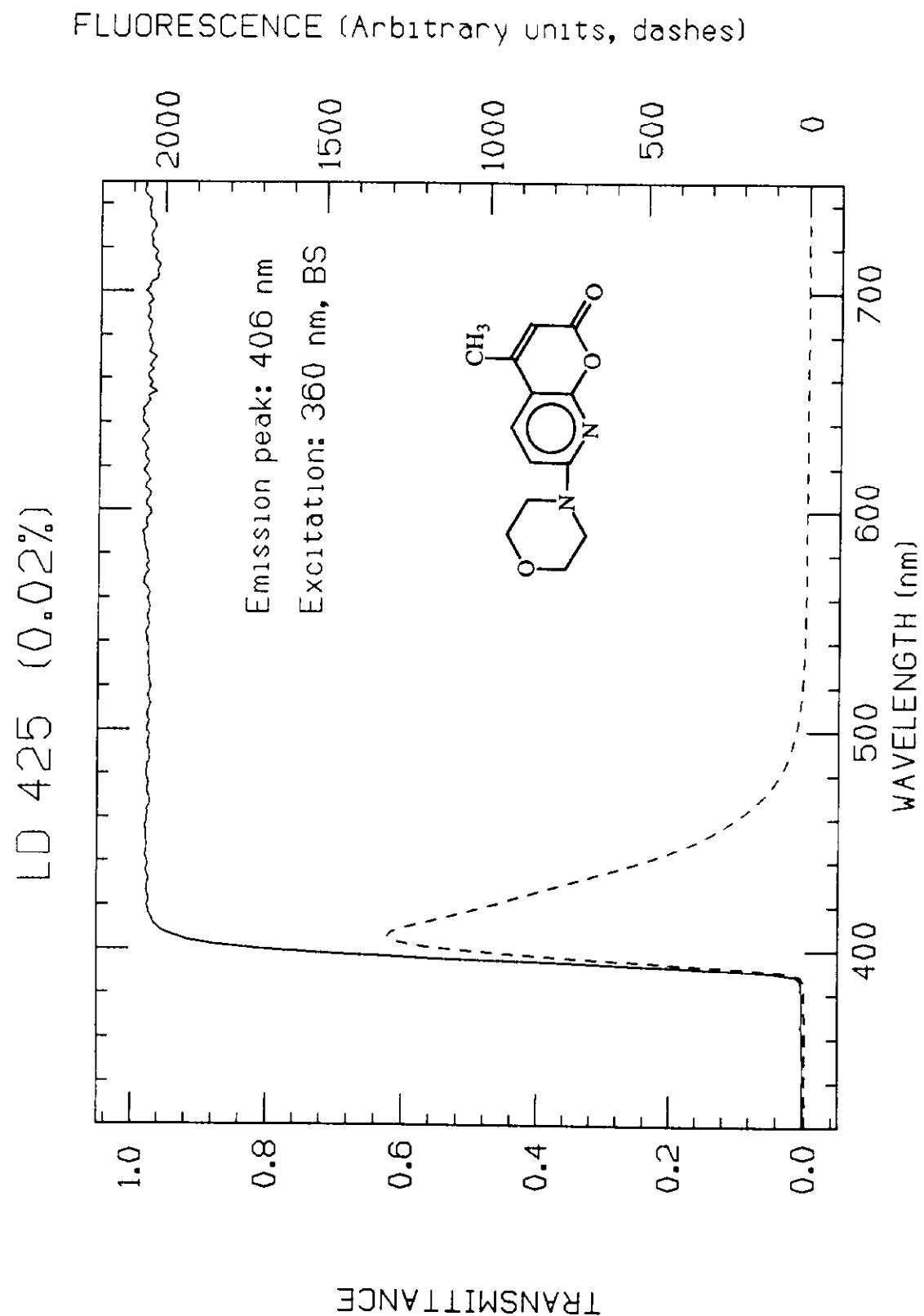


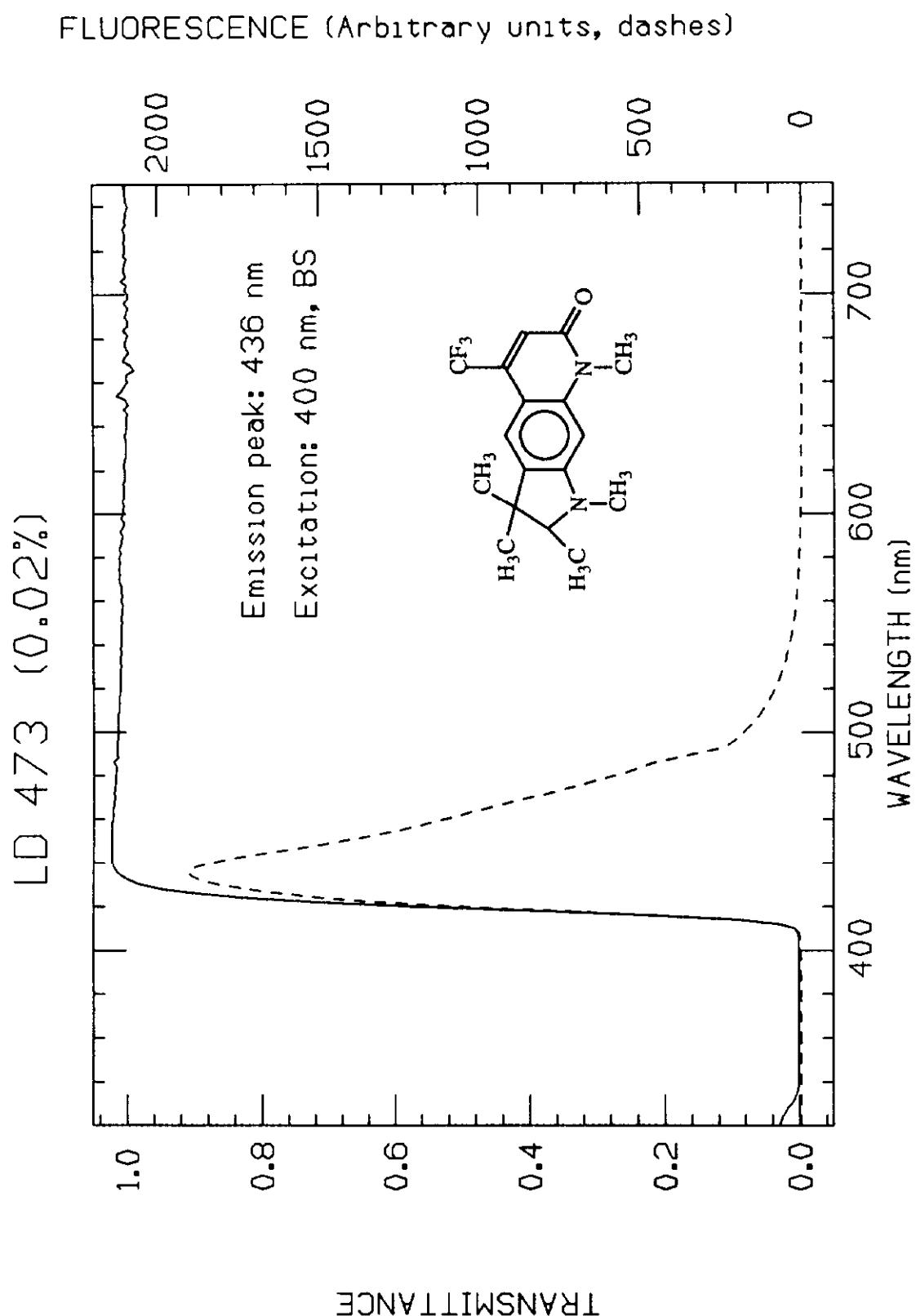


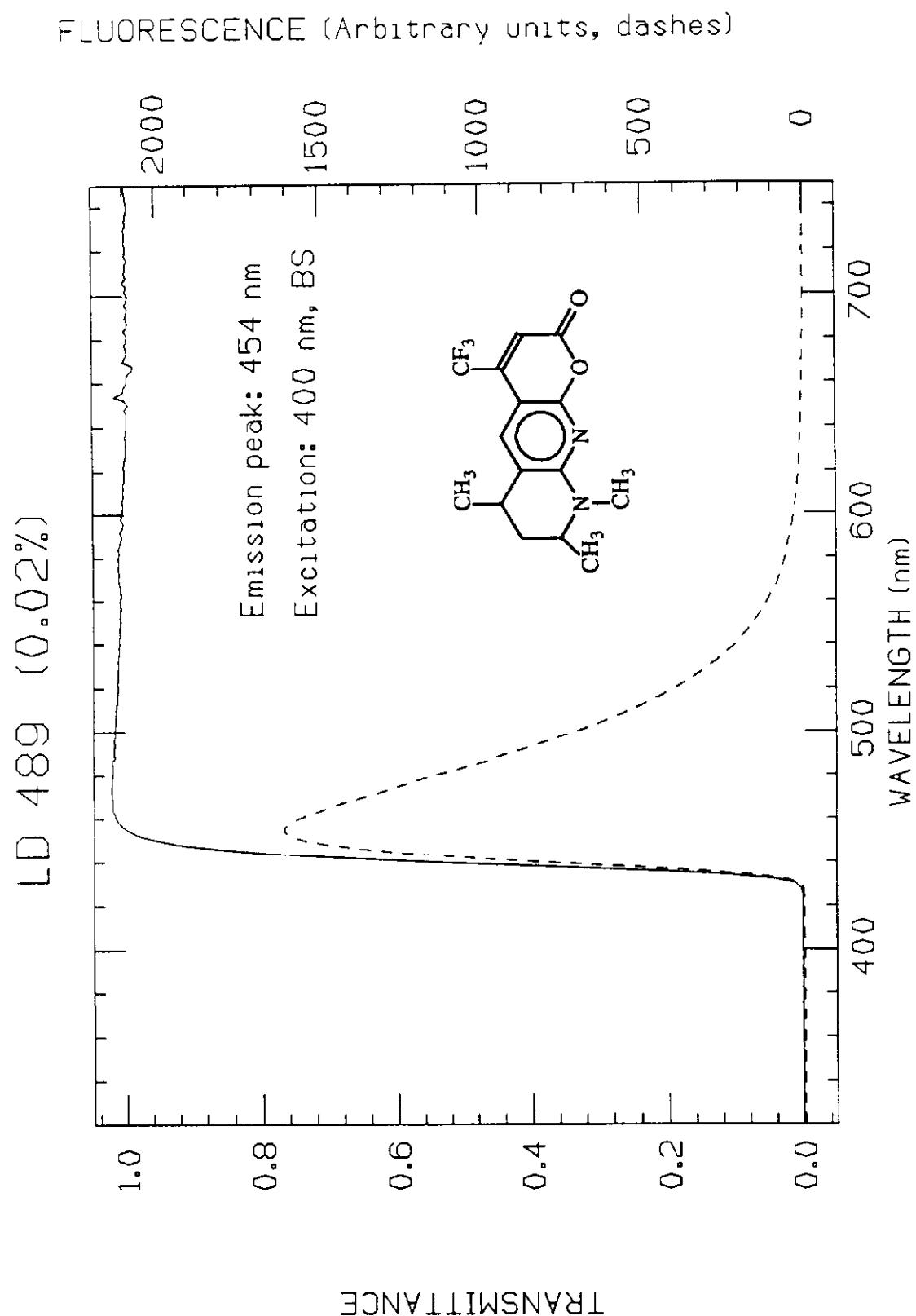


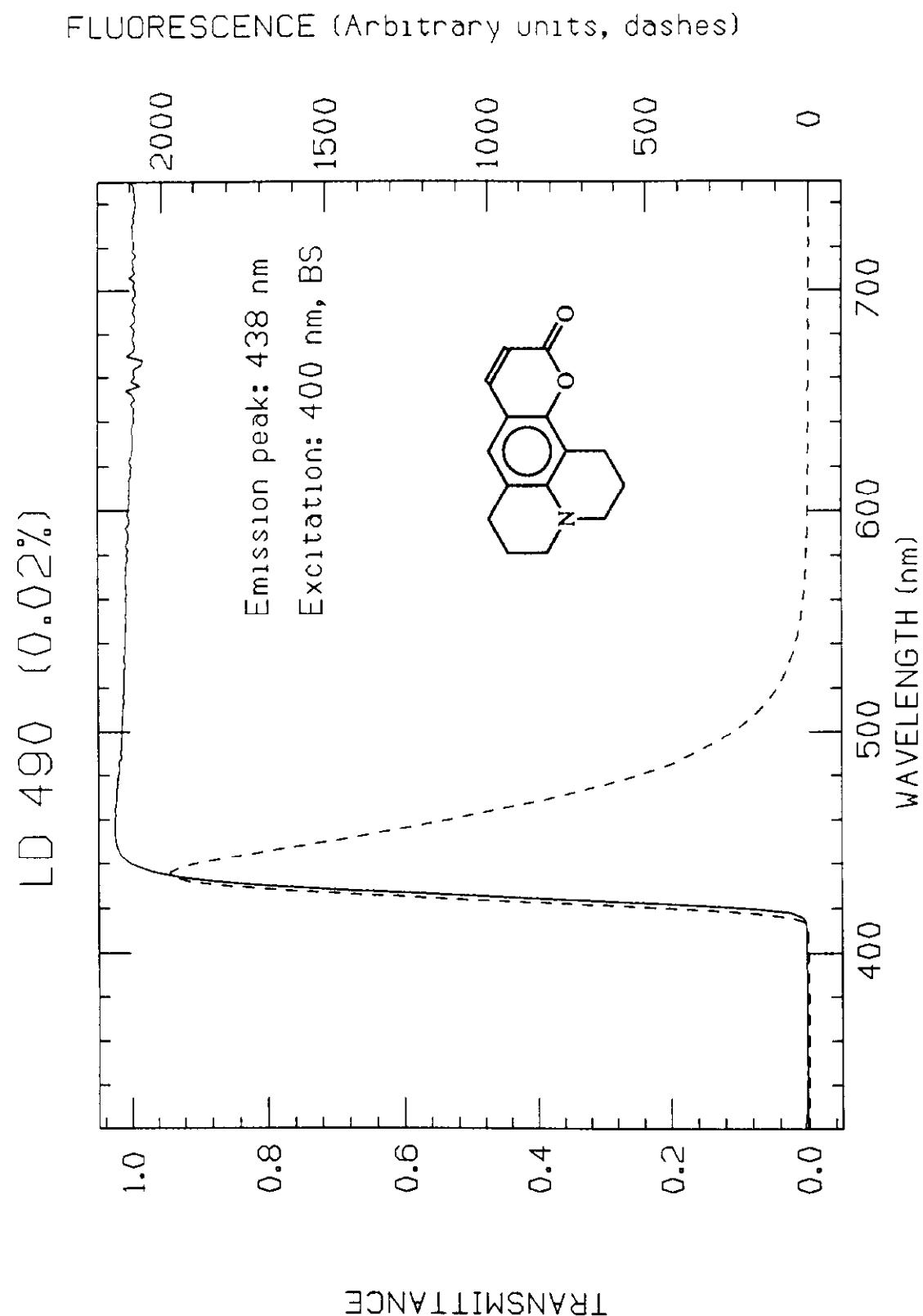


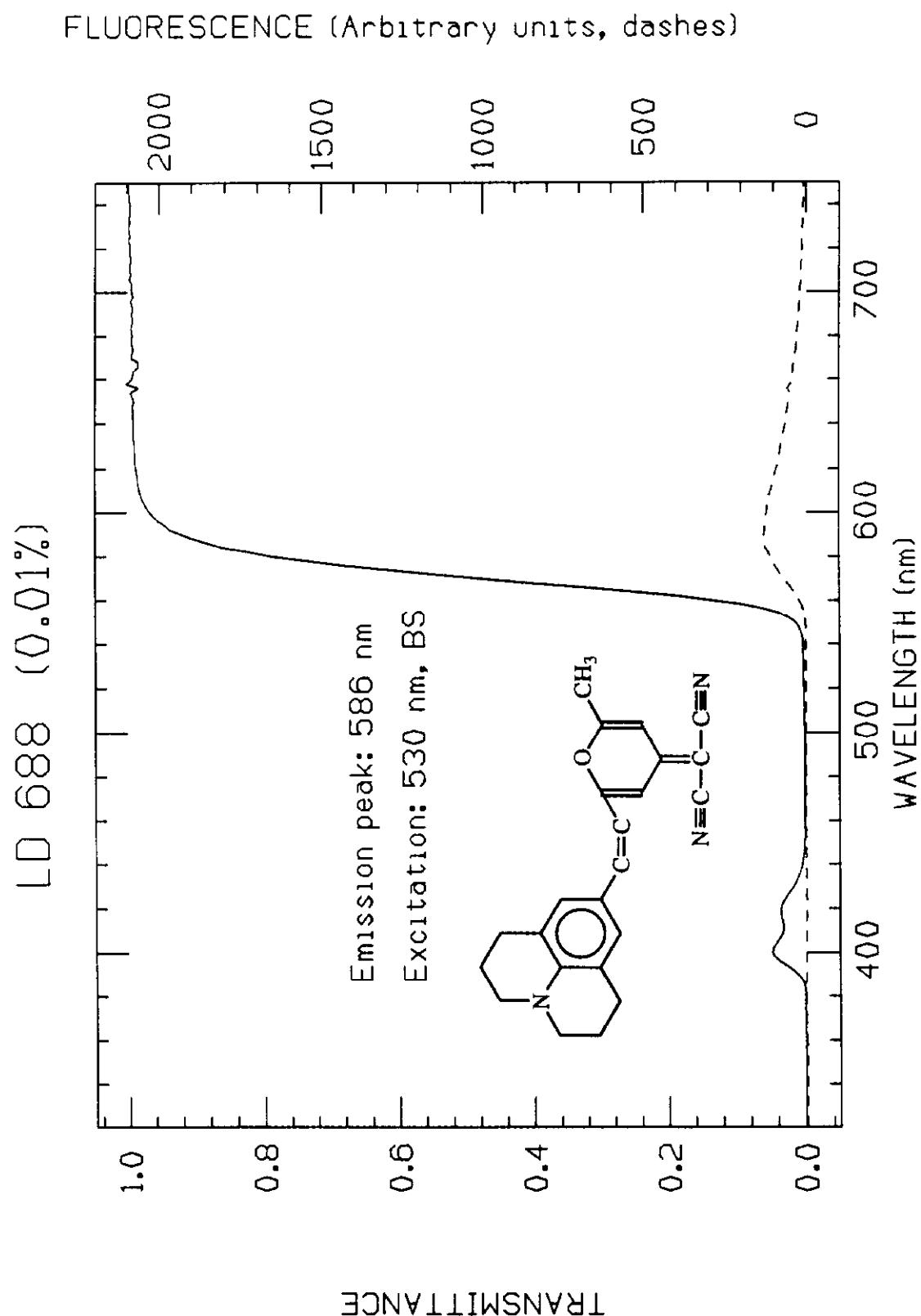


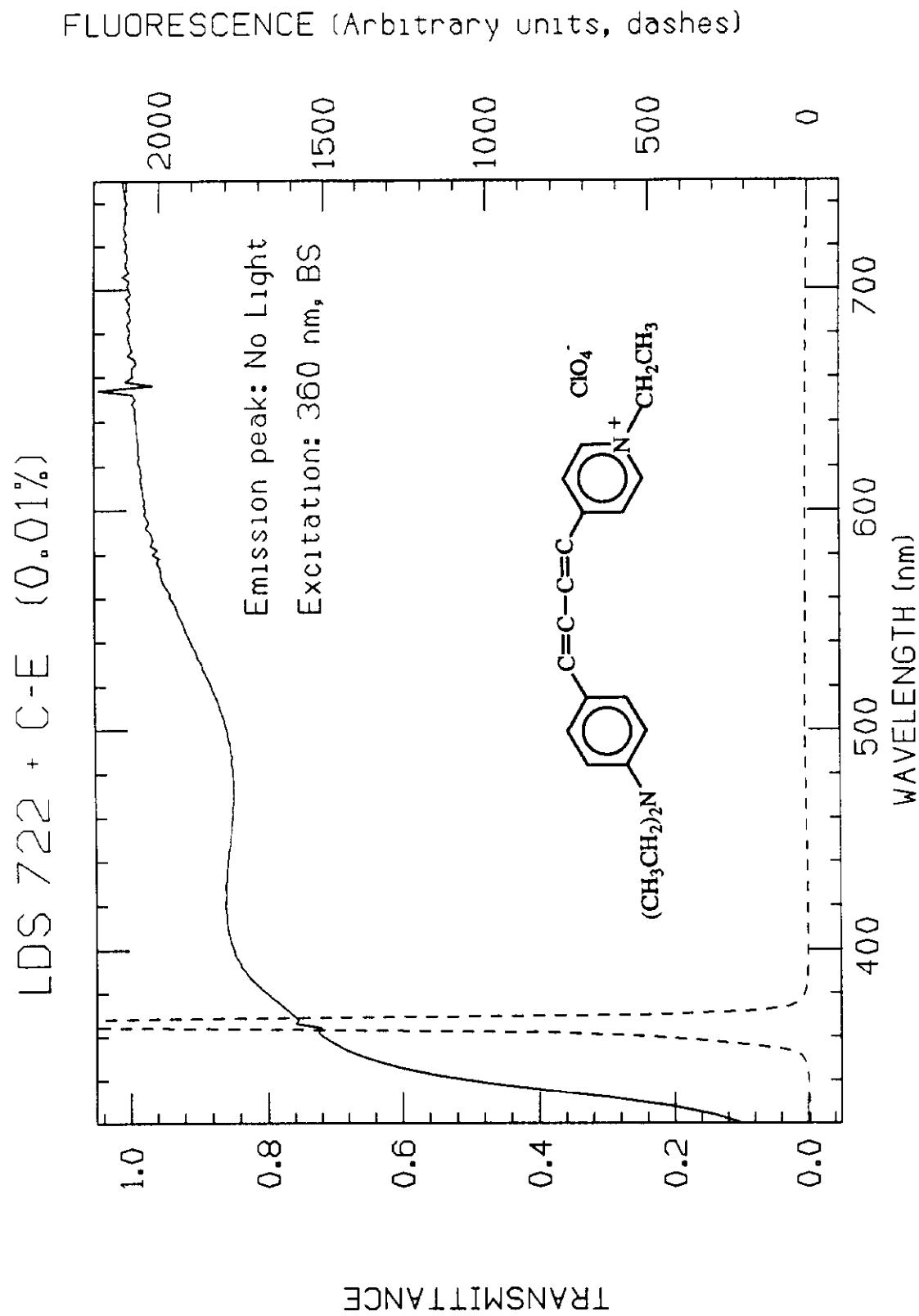


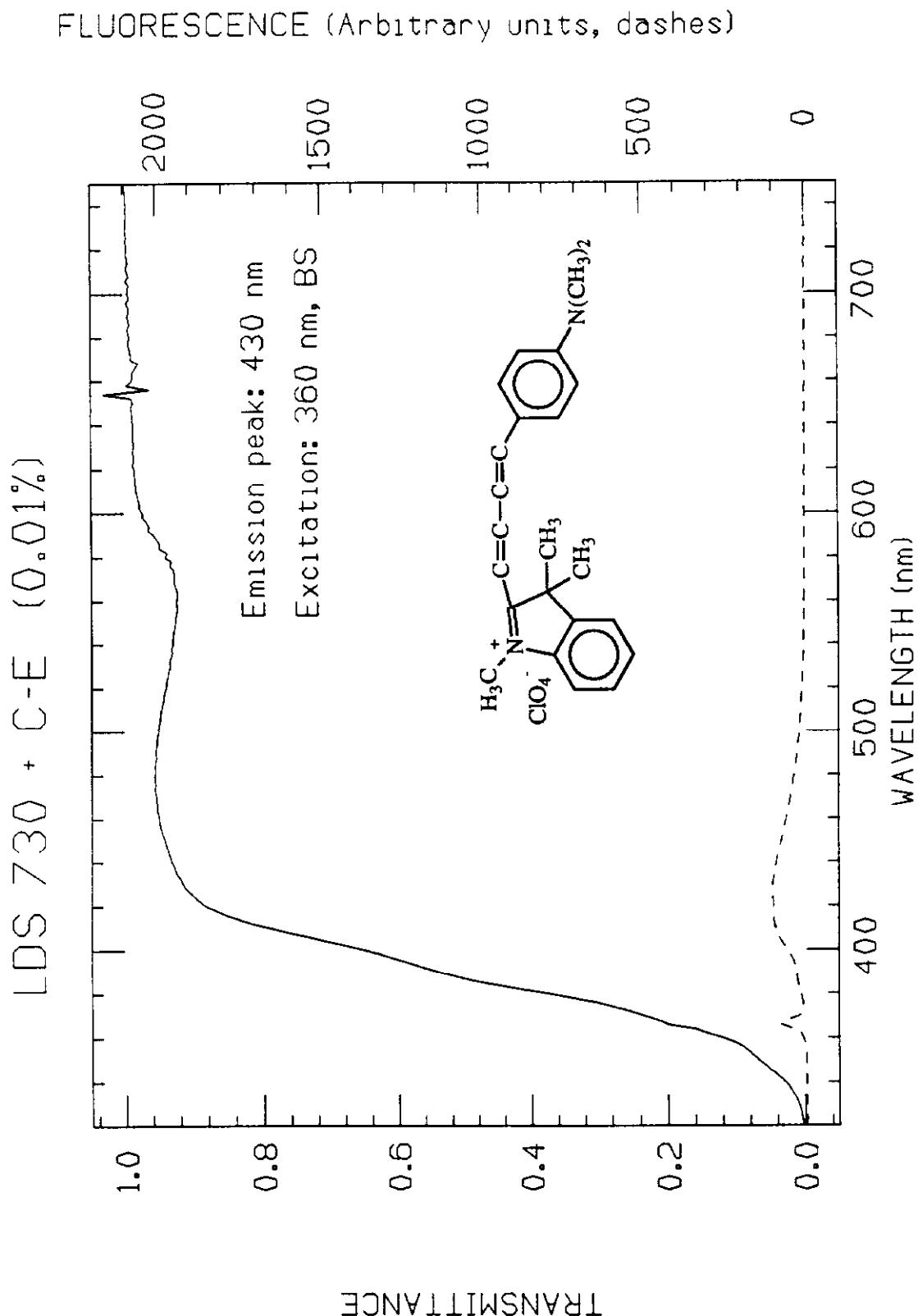


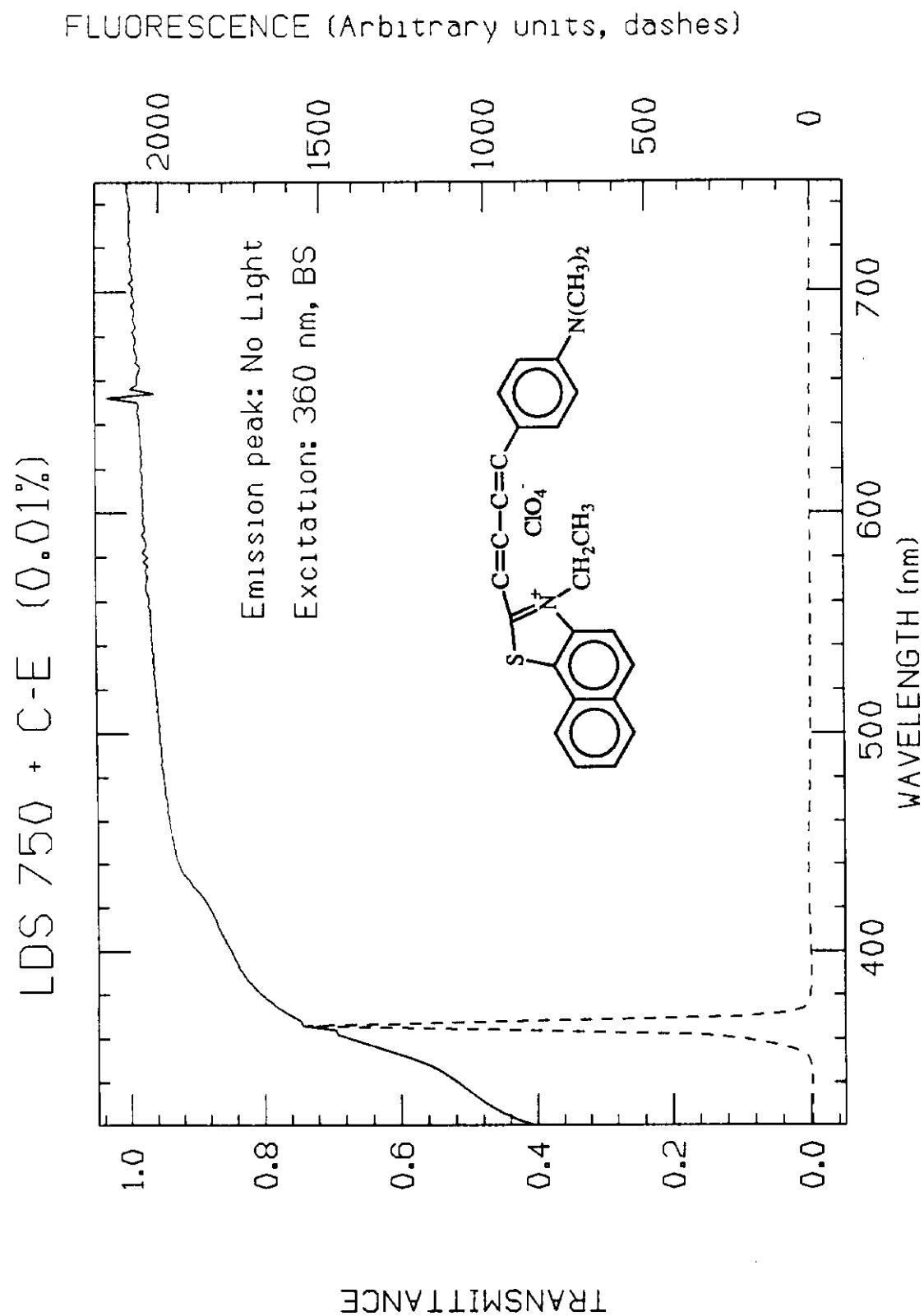


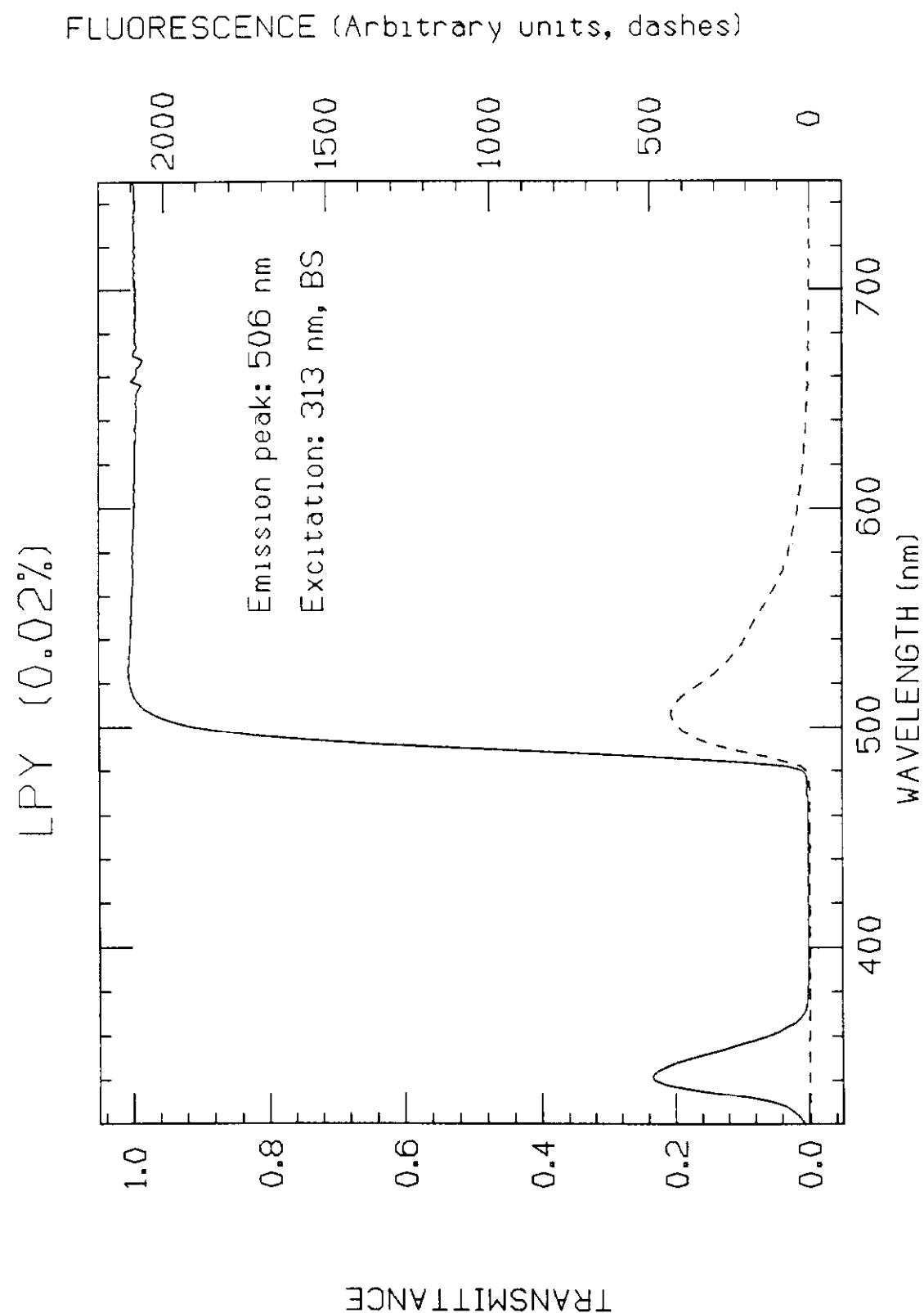


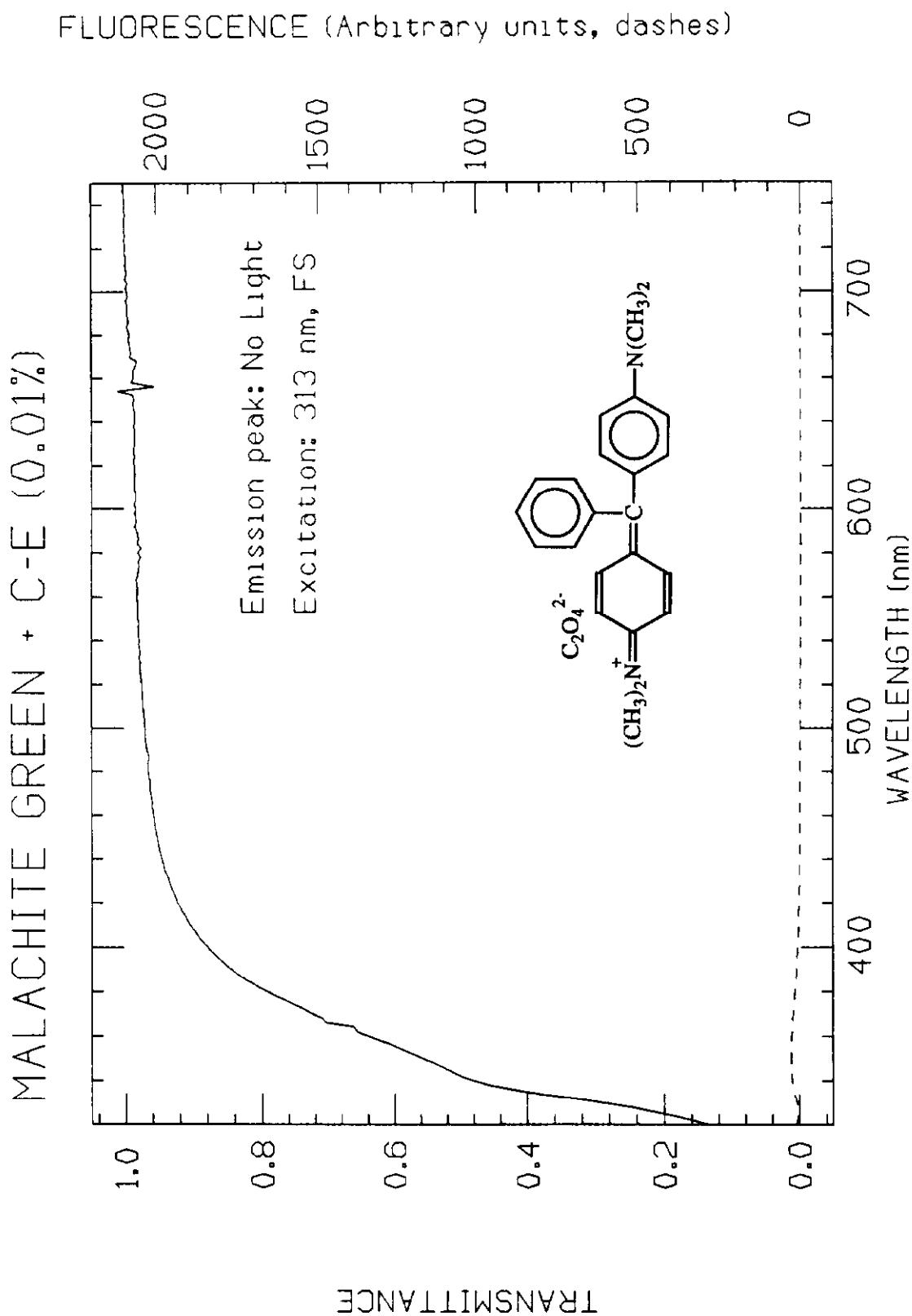


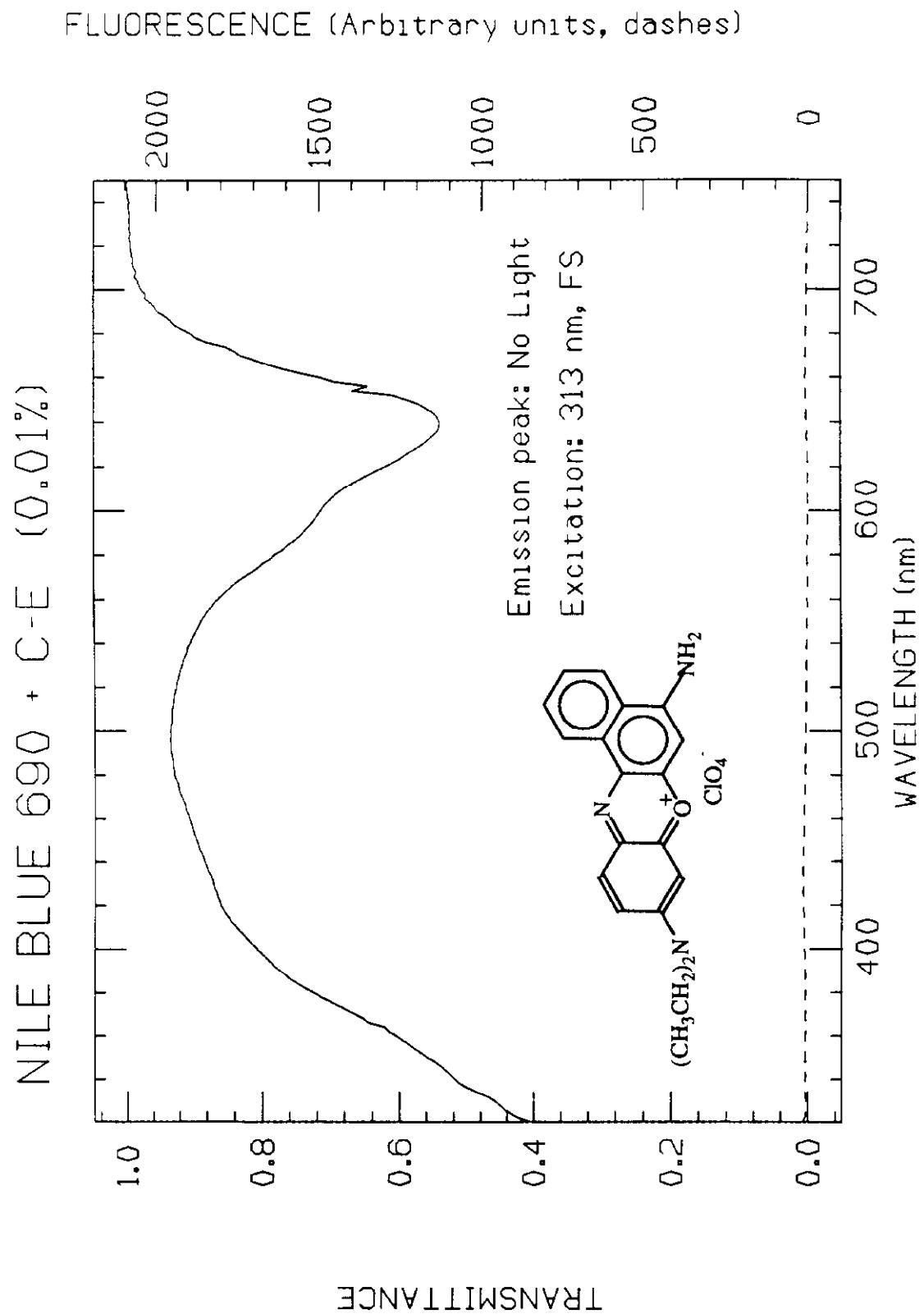


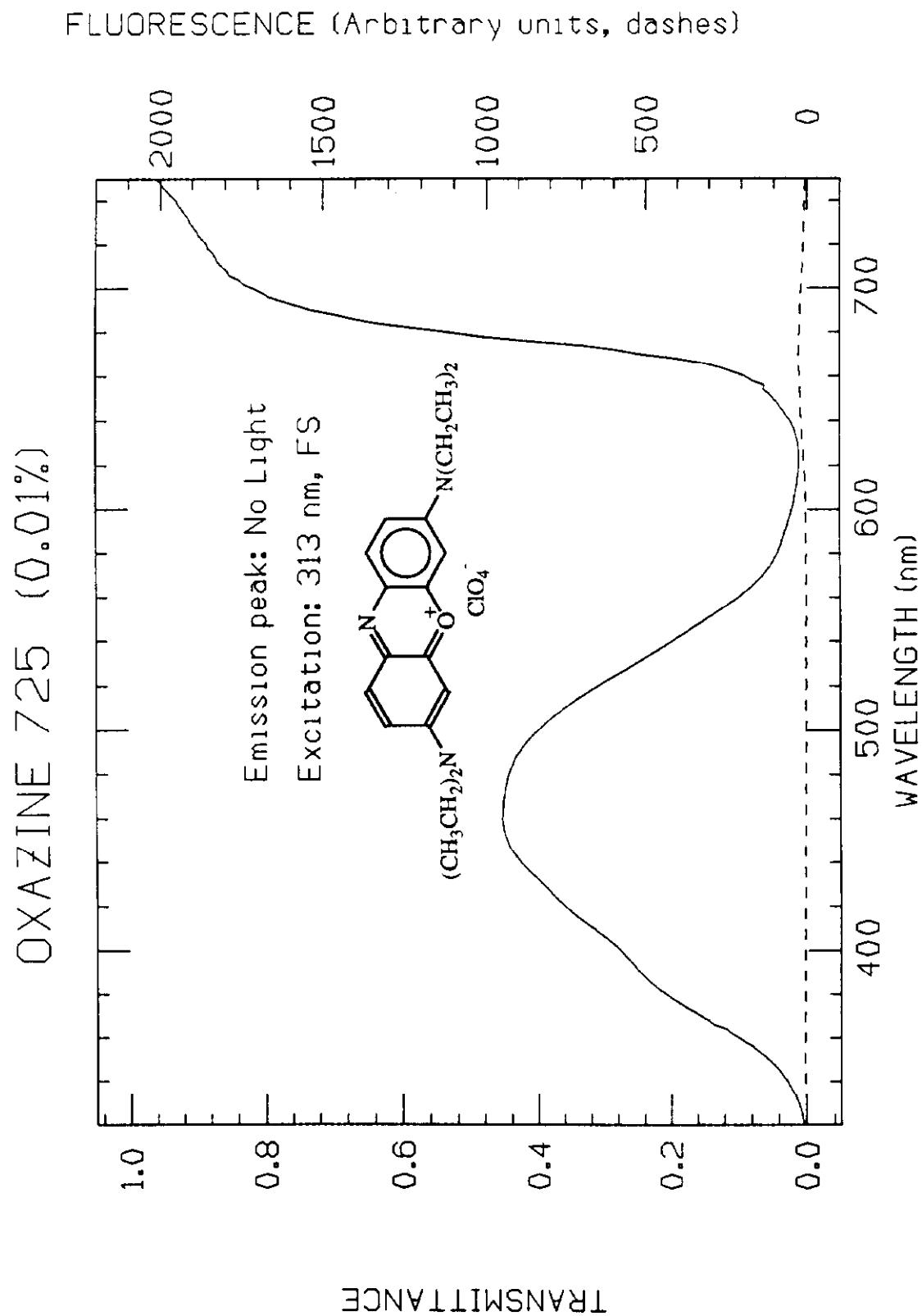


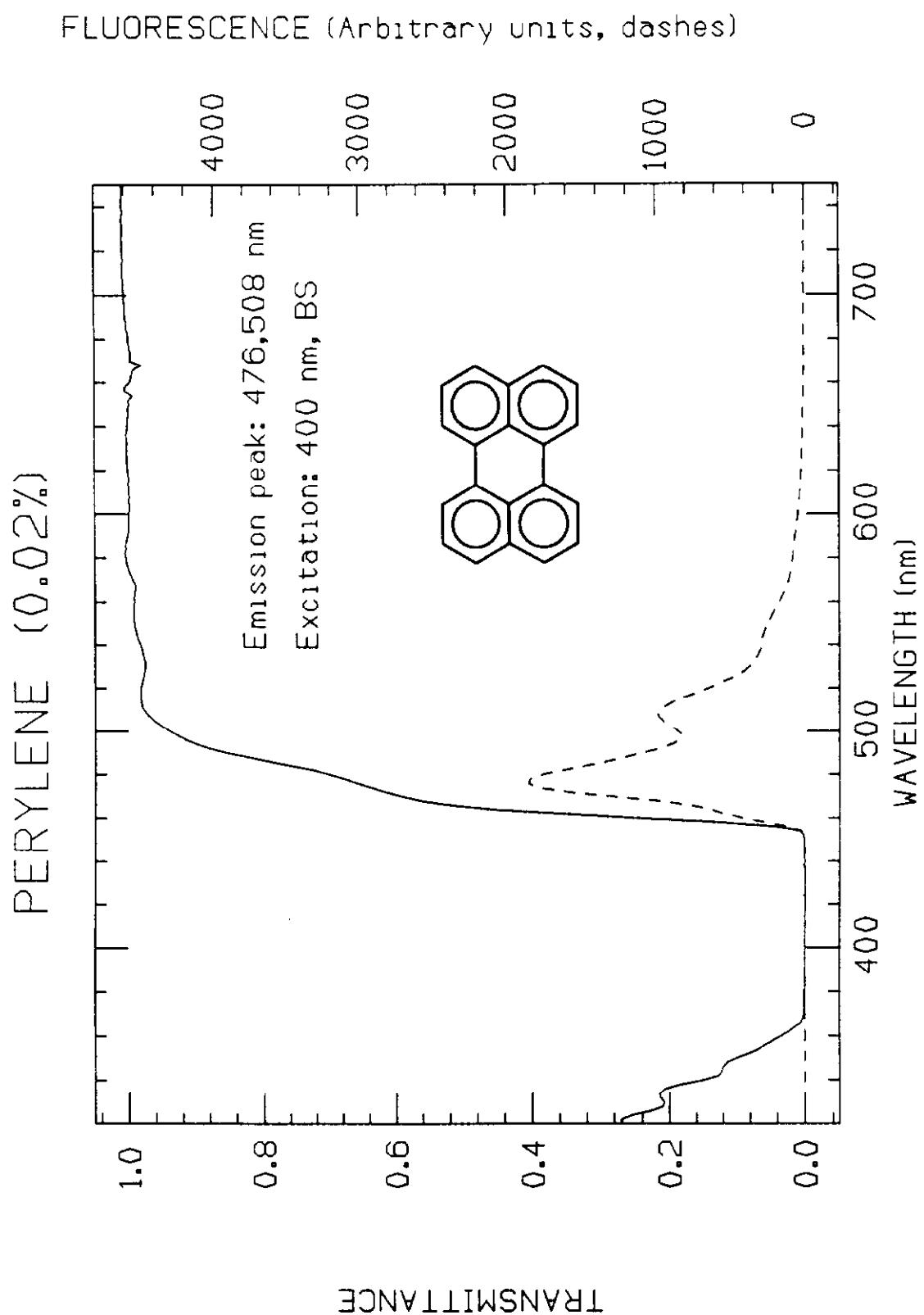


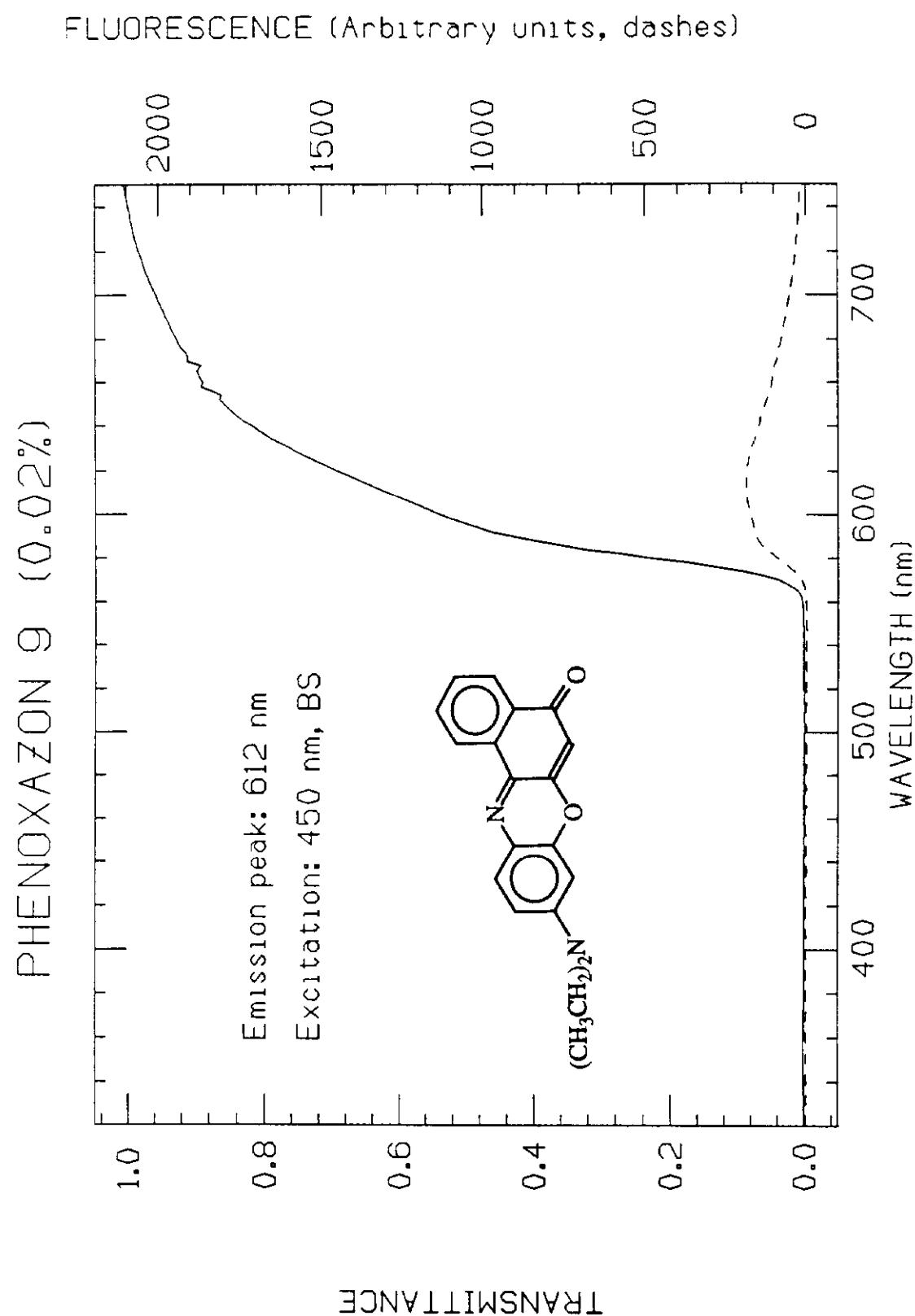


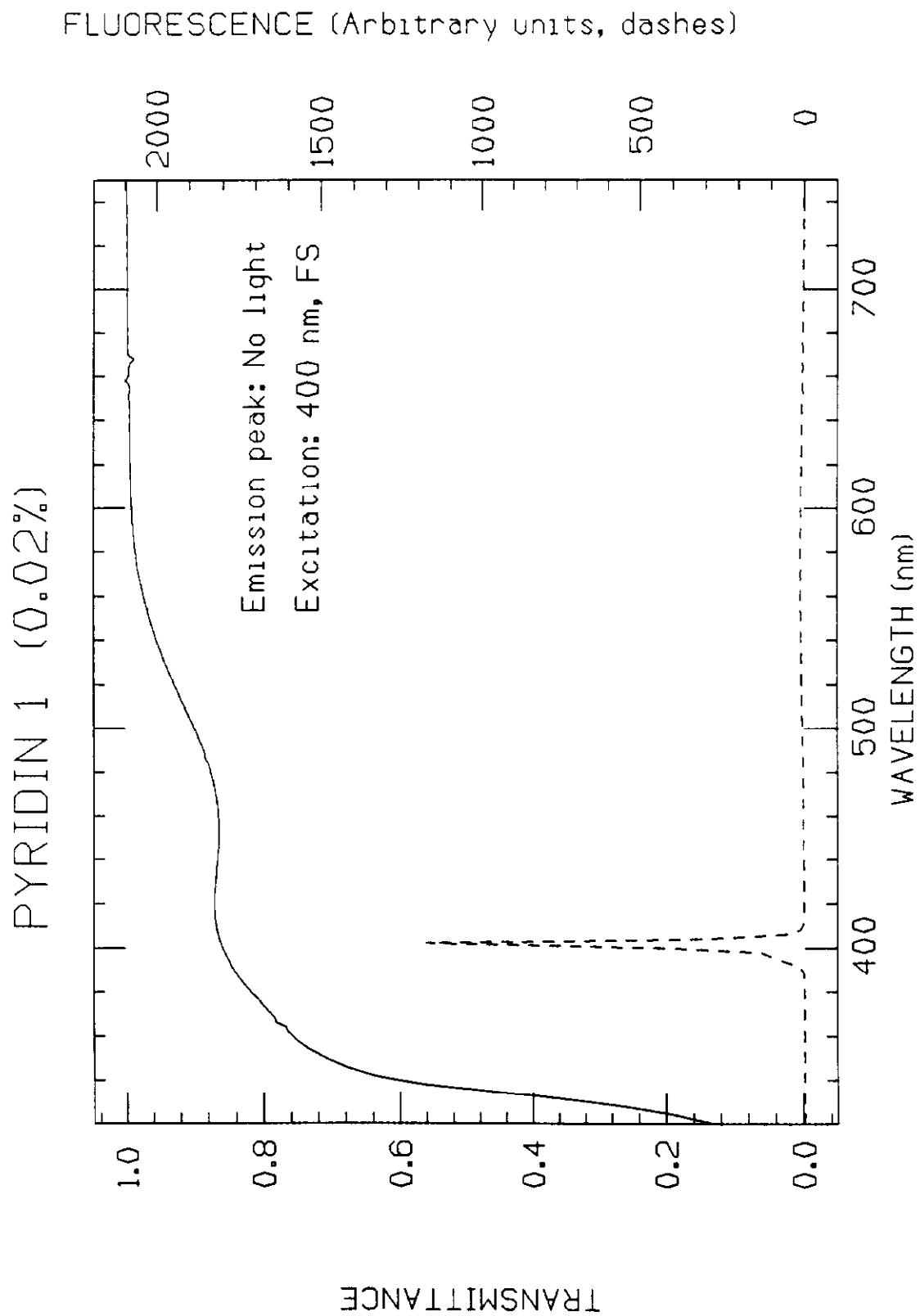


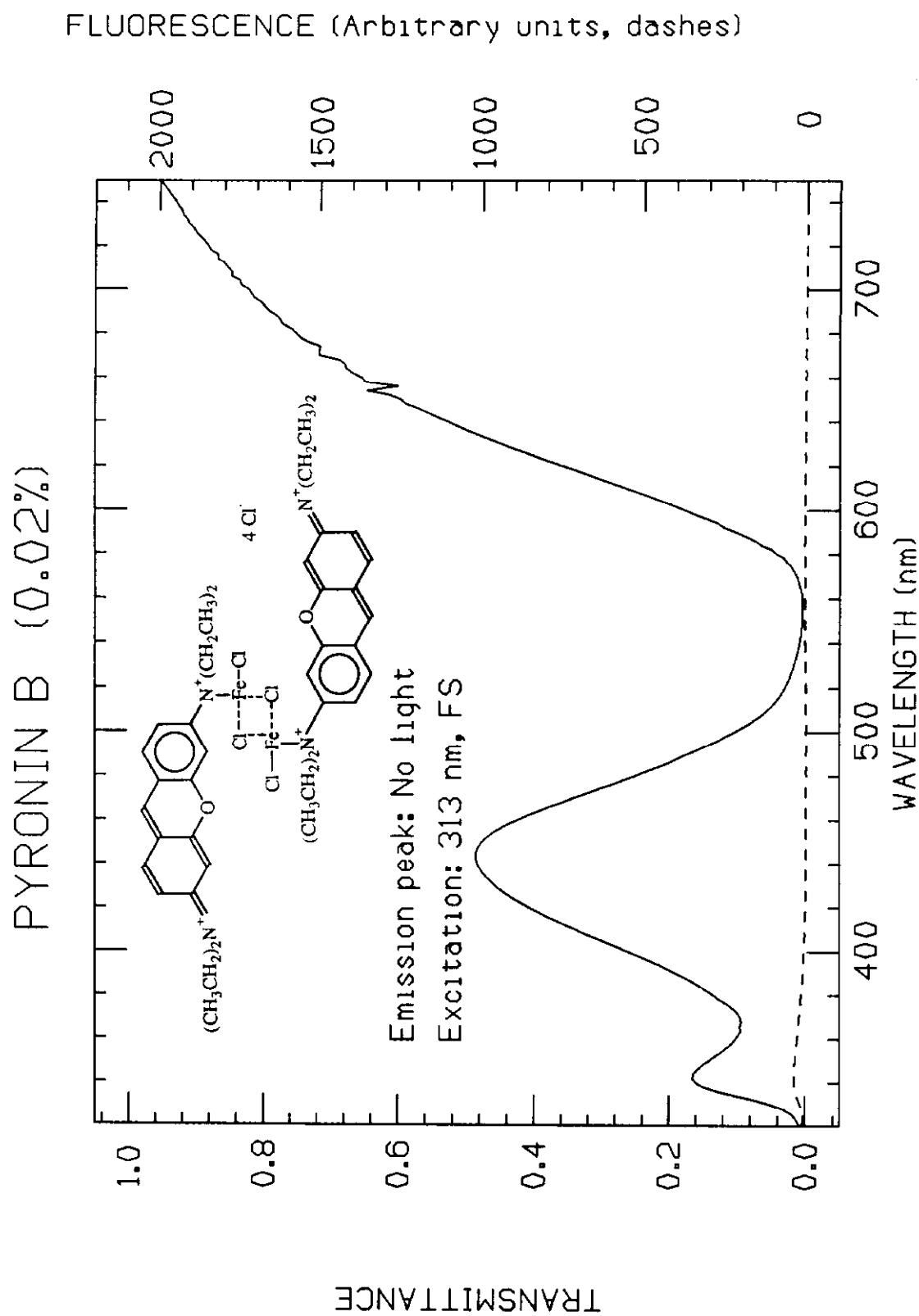


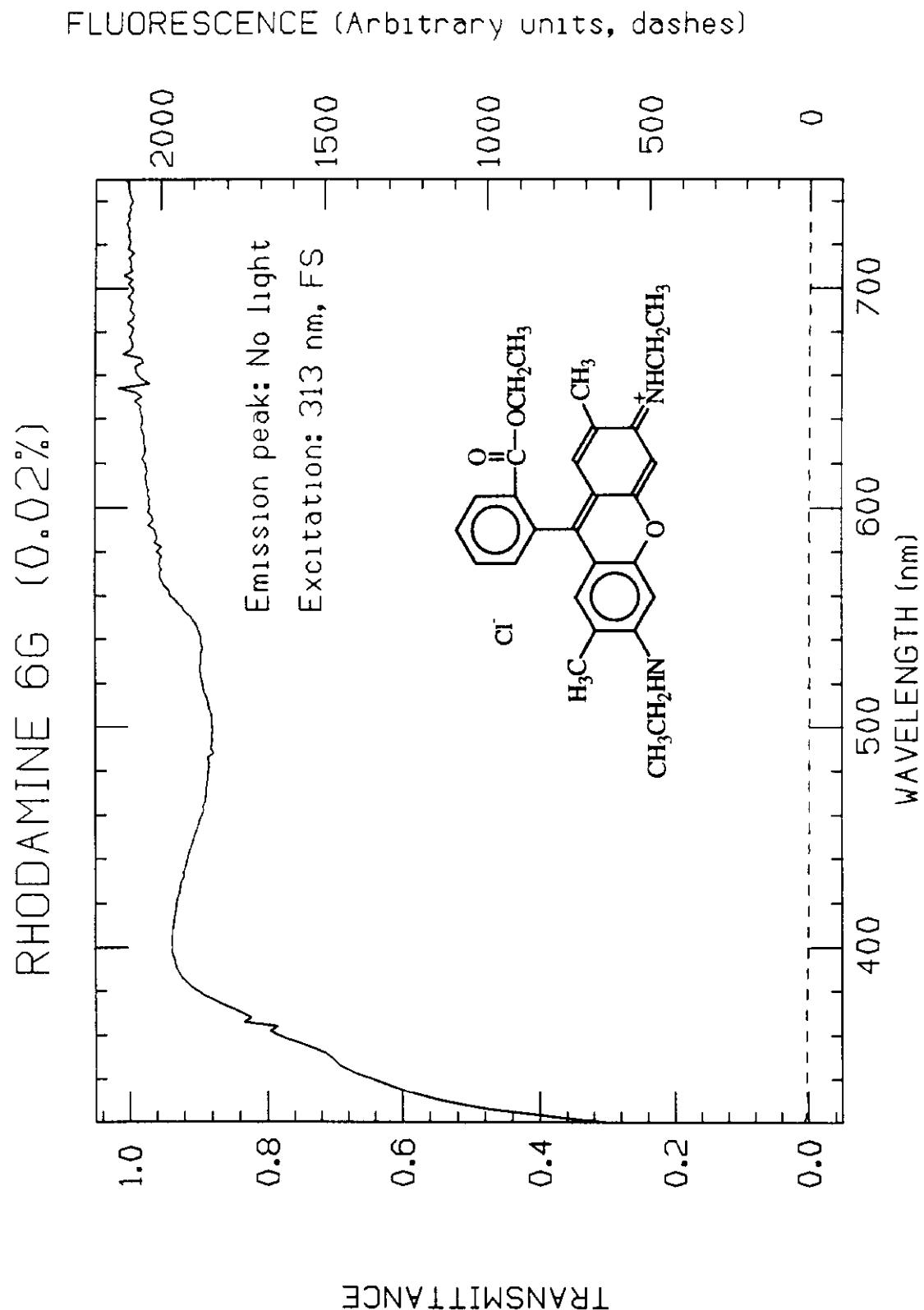


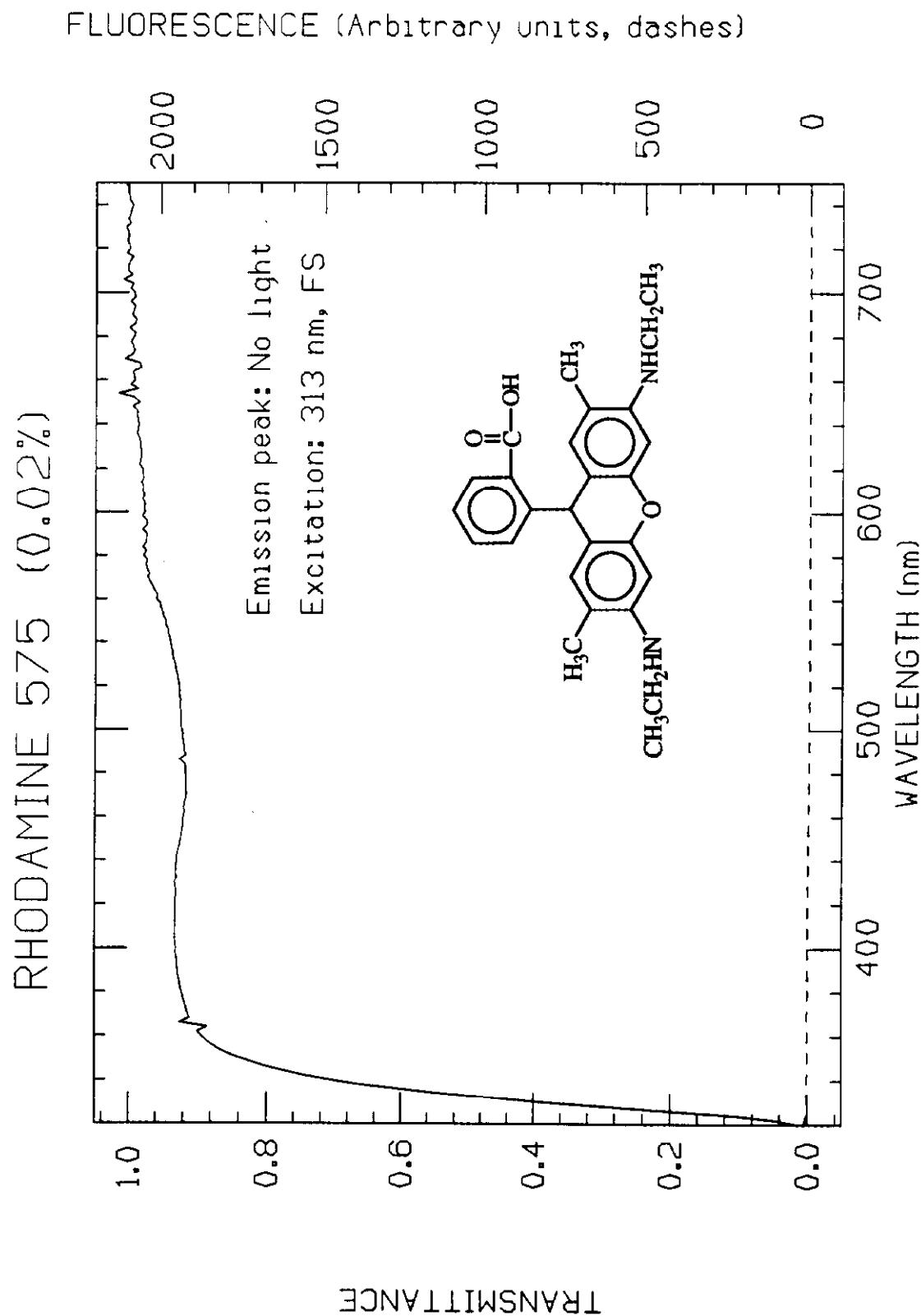


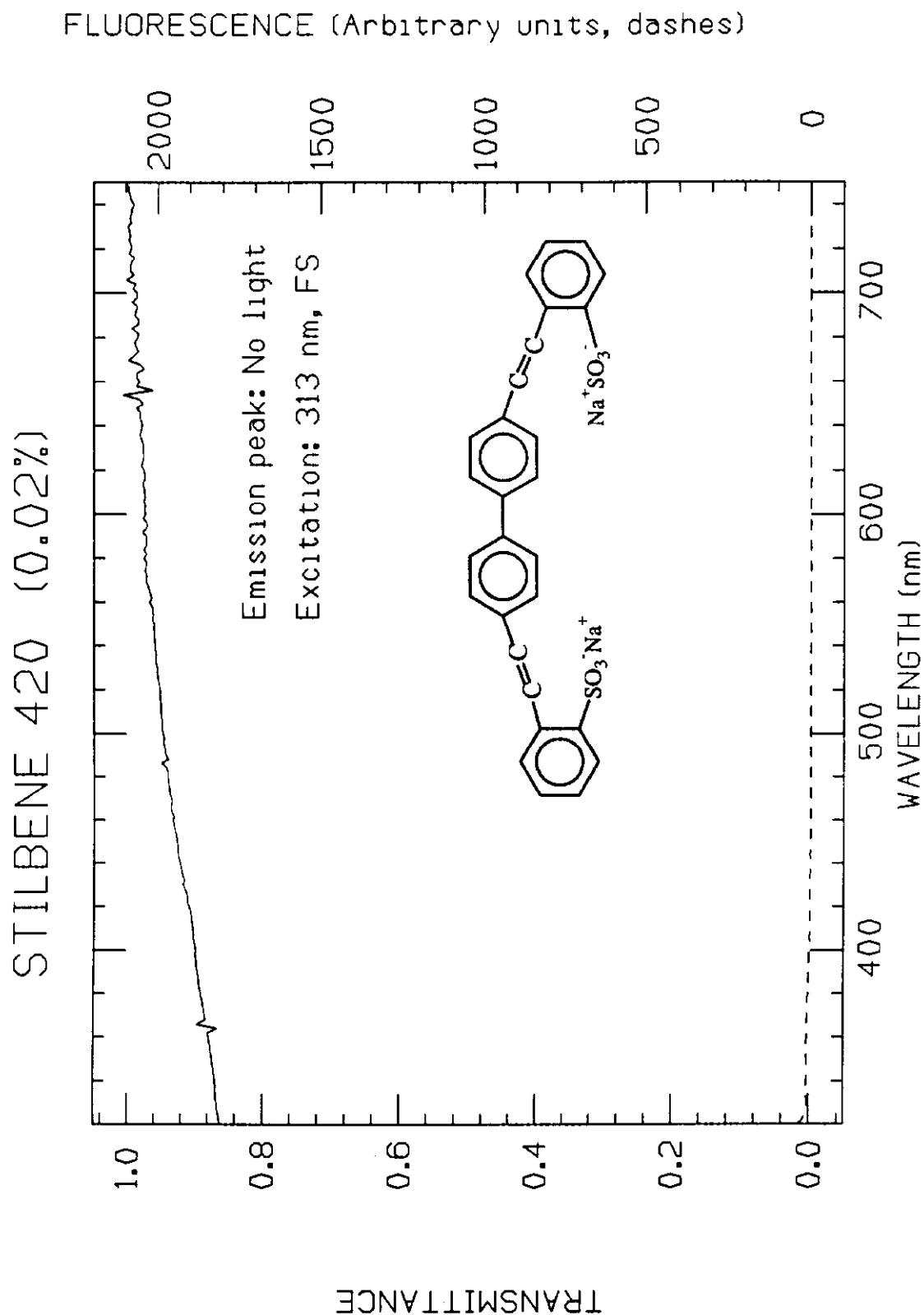












APPENDIX A: LIST OF DOPANT NAMES

DOPANTS	CAS #	NAME
ACRIDINE O B	494-38-2	3,6-bis(dimethylamino)acridine
ACRIDINE Y	135-49-9	3,6-diamino-2,7-dimethylacridine hydrochloride
ACRIFLAVINE	8048-52-0	acriflavinium chloride
BBOT	7128-64-5	2,5-bis(5'-tertbutyl)-benzoxazoly-(2')-thiophene
bis-MSB	13280-61-0	1,4-bis(2-methylstyryl)benzene
BSFL	*	brillantsulfafawin
C4	90-33-5	7-hydroxy-4-methyl-2-oxo-2H-1-benzopyran
C35/C481	41934-47-8	7-(diethylamino)-4-(trifluoromethyl)-2H-1-benzopyran-2-one
C138	62669-74-3	7-(dimethylamino)-2-3-dihydrocyclopenta[c][i]benzopyran-4(1H)-one
C153K/C153LP	53518-18-6	2,3,6,7-tetrahydro-9-(trifluoromethyl-1H,5H,11H-[1]benzopyran)[6,7,8-ij]quinolizine-11-one
C311	87-01-4	7-dimethylamino-4-methylcoumarin
C314T	113869-06-0	2,3,6,7-tetrahydro-1,1,7-tetramethyl-11-oxo-1H,5H,11H(1)benzopyran(6,7,8-ij)quinolizine-10-carboxylic acid ethyl ester
C338	62669-75-4	1,1-dimethylethyl-2,3,6,7-tetrahydro-11-oxo-1H,5H,11H(1)benzopyran(6,7,8-ij)quinolizine-10-carboxylate
C339	62669-73-2	6,7,8,9-tetrahydro-4-methyl-2H-pyrano-[3,2-g]quinolin-2-one
C440	26093-31-2	7-amino-4-methyl-2H-1-benzopyran-2-one
C445	28821-18-3	7-(ethylamino)-4-methyl-2H-1-benzopyran-2-one
C450	26078-25-1	7-(ethylamino)-4,6-dimethyl-2H-1-benzopyran-2-one
C460	91-44-1	7-(diethylamino)-4-methyl-2H-1-benzopyran-2-one
C466/LD466	20571-42	7-(diethylamino)-2H-1-benzopyran-2-one
C478	41175-45-5	2,3,6,7,10,11-hexahydro-1H,5H-cyclopenta[3,4][1]benzopyran[6,7,8-ij]quinolizin-12(9H)-one
C480	41267-76-9	2,3,6,7-tetrahydro-9-methyl-1H,5H,11H-[1]benzopyran[6,7,8-ij]quinolizine-11-one
C485	53518-14-2	7-(dimethylamino)-4-(trifluoromethyl)-2H-1-benzopyran-2-one
C487	*	.
C490	53518-15-3	7-amino-4-(trifluoromethyl)-2H-1-benzopyran-2-one
C498	87331-48-4	2,3,6,7-tetrahydro-10-(methylsulfonyl)-1H,5H,11H-[1]benzopyran[6,7,8-ij]quinolizin -11-one
C500	52840-38-7	7-(ethylamino)-4-(trifluoromethyl)-2H-1-benzopyran-2-one
C503	55804-70-1	7-(ethylamino)-6-methyl-4-(trifluoromethyl)-2H-1-benzopyran-2-one
C504	55804-66-5	ethyl-2,3,6,7-tetrahydro-11-oxo-1H,5H,11H(1)benzopyran(6,7,8-ij)quinolizine-10-carboxylate
C510	87349-92-6	2,3,6,7-tetrahydro-10-(3-pyridinyl)-1H,5H,11H-[1]benzopyran[6,7,8-ij]quinolizin-11-one
C515	41044-12-6	7-(dimethylamino)-3-(1-methyl-1H-benzimidazol-2-yl)-2H-1-benzopyran-2-one

DOPANTS	CAS #	NAME
C519	55804-65-4	2,3,6,7-tetrahydro-11-oxo-1H,5H,11H-[1]benzopyran-6,7,8-ij]quinolizine-10-carboxylic acid
C521	55804-67-6	10-acetyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]benzopyran-6,7,8-ij]quinolizin-11-one
C522	53518-19-7	6,7,8,9-tetrahydro-9-methyl-4-(trifluoromethyl)-2H-pyranol[3,2-g]quinolin-2-one
C523	55804-68-7	2,3,6,7-tetrahydro-11-oxo-1H,5H,11H-[1]benzopyran-6,7,8-ij]quinolizine-10-carbonitrile
C525	87331-47-3	10-(2-benzoxazolyl)-2,3,6,7-tetrahydro-1H,5H,11H-[1]benzopyran-6,7,8-ij]quinolizin-11-one
C535	27425-55-4	3-(1H-benzimidazole-2-yl)-7-(diethylamino)-2H-[1]benzopyran-2-one
C540	38215-36-0	3-(2-benzothiazolyl)-7-(diethylamino)-2H-[1]benzopyran-2-one
C545	85642-11-1	10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1H,5H,11H-[1]benzopyran-6,7,8-ij]quinolizin-11-one
CBSTY 3	*	7-dimethylamino-4-methylquinolone-2
CBSTY 124	19840-99-4	7-amino-4-methyl-2(1H)-quinolinone
DASBTI	*	*
DASP	*	*
DCI-2	*	*
DCM/DCM2	51325-91-8	[2-{[2-[4-(dimethylamino)phenyl]ethenyl]-6-methyl-4H-pyran-4-ylidene}-propanedinitrile
DiACFN	596-09-8	fluorescein diacetate
DiBFRFN	596-03-2	4',5'-dibromo fluorescein
DMETCI	*	dimethyl-9-ethylthiacarbocyanine iodide
DMPOPOP	3073-87-8	1,4-bis(4-methyl-5-phenyloxazol-2-yl)-benzene
DOCl	*	diethyloxacarbocyanine iodide
DODCI	14806-50-9	3-ethyl-2-[5-(3-ethyl-2(3H)-benzoxazolylidene)-1,3-pentadienyl]-benzoxazolium iodide
DQOCl	*	diethylthiacarbocyanine iodide
DTCI	514-73-88	3-ethyl-2-[5-(3-ethyl-2(3H)-benzothiazolylidene)-1,3-pentadienyl]-benzothiazolium iodide
DTDCl		
F555	19125-99-6	2-butyl-6-(butylamino)-1H-benz[e]isoquinoline-1,3(2H)-dione
FN548/DiCLFN	76-54-0	2',7-dichloro-3',6'-dihydroxy-spiro[isobenzofuran-1(3H),9'-xanthan-3-one]
HIDC IODIDE	36536-22-8	2-[5-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-1,3-pentadienyl]-1,3,3-trimethyl-3H-indolium iodide
ISCNFN	3326-32-7	fluorescein Isothiocyanate Isomer I
KITON RED 620	2609-88-3	N-[6-(diethylamino)-9-(2,4-disulfophenyl)-3H-xanthan-3-ylidene]-N-ethyl-ethanaminium hydroxide
LD423	58336-37-1	1,2,3,8-tetrahydro-1,2,3,3,5-pentamethyl-7H-pyrrol[3,2-g]quinolin-7-one
LD425	57980-07-1	4-methyl-7-(4-morpholinyl)-2H-pyranol[2,3-b]pyridin-2-one

DOPANTS	CAS #	NAME
LD473	58721-74-7	1,2,3,8-tetrahydro-1,2,3,3,8-pentamethyl-5-(trifluoromethyl)-7H-pyrrolo[3,2-g]quinolin-7-one
LD489	62377-37-1	6,7,8,9-tetrahydro-6,8,9-trimethyl-4-(trifluoromethyl)-2H-pyran[2,3-b][1,8]naphthyridin-2-one
LD490	58336-35-9	2,3,6,7-tetrahydro-1H,5H,[1]benzopyran[6,7,8-ij]-quinoliz-11-one
LD688	51325-95-2	2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzol[ij]quinolizn-9-yl)ethenyl]-4H-pyran-4-yldene] propanedinitrile
LDS722	89846-21-9	4-[4-[4-(dimethylamino)phenyl]-1,3-butadienyl]-1-ethyl-pyridinium perchlorate
LDS730	76433-27-7	2-[4-[4-(dimethylamino)phenyl]-1,3-butadienyl]-1,3,3-trimethyl-3H-indolium perchlorate
LDS750	89872-07-1	2-[4-[4-(dimethylamino)phenyl]-1,3-butadienyl]-3-ethylnaphtho[2,1-d]thiazolium perchlorate
LPY	*	*
MALACHITE GREEN	18015-76-4	N-[4-[[4-(dimethylamino)phenyl]phenyl]methylene]-2,5-cyclohexadien-1-ylidene-N-methylnaphthalimium ethanedioate(2:2:1)
NILE BLUE	53340-16-2	5-amino-9-(diethylamino)-benzo[a]phenoxazin-7-ium perchlorate
OXAZINE 725	24796-94-9	3,7-bis(diethylamino)-phenoxyazin-5-ium perchlorate
PERYLENE PHENOXAZON 9 PYRIDIN1 PYRONIN B	198-55-0 7385-67-3 *	dibenz(de,k)anthracene nile red *(6-diethylamino)-3H-xanthan-3-ylidine)diethylammonium chloride
RHODAMINE 6G	2150-48-3	(6-diethylamino)-3H-xanthan-3-ylidine)diethylammonium chloride
RHODAMINE575	989-38-8	9-(2-(ethoxycarbonyl)phenyl)-3,6-bis(ethylamino)-2,7-dimethylxanthylum chloride
STILBENE 420	25152-49-2	2-[6-(ethylamino)-3-(ethylamino)-2,7-dimethyl-3H-xanthan-9-yl]-benzoic acid
	27344-41-8	2,2'-(1,1'-biphenyl)-4,4'-diyldi-2,1-ethenediyli)bis-benzenesulfonic acid disodium salt

* information not available in MSDS

APPENDIX B: LIST OF FLUORESCENCE MEASUREMENTS

DOPANTS	RADAM#	POLY#	F 313	F 360	B 360	F 400	B 400	F 436	B 436	F 450	B 450
LD489	-										
LD490	22	77	X	X	X	X	X	X	X	X	X
LD688	22	11	X	X	X	X	X	X	X	X	X
LDS722+C-E	22	11	X	X	X	X	X	X	X	X	X
LDS730+C-E	22	11	X	X	X	X	X	X	X	X	X
LDS750+C-E	22	11	X	X	X	X	X	X	X	X	X
LPY	20	81	X♦								
MALACT GR.+C-E	22	11	X								
NILE BLUE 690+C-E	22	11	X								
OXAZINE 725	22	11	X								
PERYLENE	22	78	X								
PHENOXAZON 9	*	78	X								
PYRIDIN 1	22	78	X								
PYRONIN B	*	79	X								
RHODAMINE 6G	22	79	X								
RHODAMINE 575	22	79	X								
STILBENE 420	22	79	X								

C-E = A crown-ether added as solubilizing agent

* Samples were too opaque to be irradiated

† Samples do not show any fluorescence.

♦ LPY was measured with a BS 313.

APPENDIX C: TABLE OF SPECTROSCOPIC CHARACTERISTICS

DOPANTS	ABS. RANGE (nm)	FS EMISSION (nm)	BS EMISSION (nm)	LIFETIME (ns)	BRIGHTNESS (%)
K27	300-480	468,496,530	496,530	11.8	100*
ACRIDINE O B	300-500	520	-	Insufficient Light Output	
ACRIDINE Y	300-560	none	none	No Light Output	
ACRIFLAVINE	300-360	none	none	No Light Output	
BBOT	300-420	414,436460	436,462	-	
bis-MSB	300-410	406,426	428	-	
BSFL	300-480	none	none	No Light Output	
C4	300-360	368	-	Insufficient Light Output	
C35/C481	300-450	456	460	9.1	95
C138	300-400	406	410	Short wavelength emission	
C153K/C153LP	300-470	478	480	10.8	99
C311	300-400	408	410	Short wavelength emission	
C314T	300-460	456	468	9.6	106
C338	300-460	460	472	9.7	105
C339	300-410	408	414	Short wavelength emission	
C440	300-390	394	396	Short wavelength emission	
C445	300-390	402	402	Short wavelength emission	
C450	300-400	402	404	Short wavelength emission	
C460	300-410	410	414	Short wavelength emission	
C466/LD466	300-420	416	420	Short wavelength emission	
C478	300-420	422	428	6.9	65
C480	300-430	424	428	7.2	63
C485	300-450	452	456	9.3	107
C487	300-420	426	430	7.2	62
C490	300-420	426	430	6.9	52

DOPANTS	ABS. RANGE (nm)	FS EMISSION (nm)	BS EMISSION (nm)	LIFETIME (ns)	BRIGHTNESS (%)
C498	300-470	456	470	9.5	109
C500	300-440	440	444	8.0	85
C503	300-440	442	446	8.1	88
C504	300-470	458	468	8.5	-
C510	300-480	478	484	7.6	119
C515	300-480	478	492	7.5	100
C519	300-490	474	488	10.0	100
C521	300-490	476	490	10.3	106
C522	300-460	466	472	9.4	113
C523	300-490	470	484	10.0	95
C525	300-520	508	518	8.1	82
C535	300-500	504	508	7.7	85
C540	300-510	510	514	7.4	90
C545	300-520	526	528	8.4	76
CBSTY 3	300-390	366,392	396	Short wavelength emission	
CBSTY 124	300-380	366,388	390	Short wavelength emission	
DASBTI	300-460	474	474	Insufficient Light Output	
DASPI	300-420	440	442	Insufficient Light Output	
DCI2	300-660	474	-	Insufficient Light Output	
DCM/DCM2	300-530	558,584	562,582	Insufficient Light Output	
DiACFN	-360	none	none	No Light Output	
DiBFRN	300-440	514	-	No Light Output	
DMETCI	300-490	none	none	No Light Output	
DMPOPOP	300-420	408,430	430	No Light Output	
DOCI	300-460	none	none	No Light Output	
DODCI	300-460	none	none	No Light Output	
DQOCl	300-580	none	none	No Light Output	
DTCl	300-500	none	none	No Light Output	

DOPANTS	ABS. RANGE (nm)	FS EMISSION (nm)	BS EMISSION (nm)	LIFETIME (ns)	BRIGHTNESS (%)
DTDCI	300-540	none	-	No Light Output	-
F555	300-480	494	496	No Light Output	-
FN548/DiCLFN	300-520	none	none	No Light Output	-
HIDC IODIDE	300-570	none	none	No Light Output	-
ISCNFN	300-330	none	none	No Light Output	-
KITON RED 620	300-380	none	none	No Light Output	-
LD 423	300-400	398	402	Short wavelength emission	-
LD 425	300-390	404	406	Short wavelength emission	-
LD 473	300-430	434	436	-	-
LD 489	300-450	452	454	-	-
LD 490	300-430	434	438	-	-
LD 688	300-600	584	586	Insufficient Light Output	-
LDS 722	300-590	none	none	No Light Output	-
LDS 730	300-600	384,424	430	Insufficient Light Output	-
LDS 750	300-400	none	none	No Light Output	-
LPY	300-510	-	506	6.9	89
MALACHITE GR	300-510	none	none	No Light Output	-
NILE BLUE	300-700	none	none	No Light Output	-
OXAZINE 725	300-720	none	none	No Light Output	-
PERYLENE	300-450	-	476,508	-	-
PHENOXAZON 9	300-600	452,476,508	572,584	Insufficient Light Output	-
PYRIDIN 1	300-380	none	612	No Light Output	-
PYRONIN B	300-760	none	none	No Light Output	-
RHODAMINE 6G	300-370	none	none	No Light Output	-
RHODAMINE 575	300-350	none	none	No Light Output	-
STILBENE 420	-320	none	none	No Light Output	-

*All brightness data relative to K27
 FS = Front Surface
 BS = Back Surface